



# GEOCHEMISTRY

A Translation of

## ГЕОХИМИЯ

o. 2

1959

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*Published by*

**The Geochemical Society**

Translated and Produced by Royer & Roger, Inc.

# GEOCHEMISTRY

A translation of the journal of the Academy of Sciences, U. S. S. R.,  
devoted to geochemistry

A publication of the Geochemical Society, supported financially by a grant from the National Science Foundation.

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Per year (eight issues) . . . . . \$20.00

To members of the Geochemical Society and to educational institutions . . . . . \$10.00

Single copies . . . . . \$2.00 and \$4.00

Subscriptions and orders should be addressed to the Geochemical Society and sent to

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## TRANSLITERATION

There is no ideal system of transliterating Russian; each has its advantages and disadvantages. For the translation of Geokhimiya we have chosen the system used by Chemical Abstracts, partly because of its wide acceptance by other journals and partly because of certain advantages in alphabetization of names. The principal differences between this system and others in common use are as follows:

Russian	Chem. Abs.	Others
Х	kh	h
Ц	ts	tz
Ш	shch	sch
Ю	yu	lu
Я	ya	ia

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## ACADEMICIAN A. E. FERSMAN

(75th Anniversary of birth)

Alexander Evgen'evich Fersman was born in Petersburg on November 8, 1883. He became interested in minerals and rocks in his childhood. When still a student at the University of Moscow he amazed his colleagues and professors by his excellent knowledge of nature. In the Department of Mineralogy at the University of Moscow, Fersman came to know V.I. Vernadskii, first as Vernadskii's student and later as his closest friend. At that time, a tremendous amount of work was being done at the Department of Mineralogy towards a genetic treatment of mineralogy and the new science of geochemistry. The new ideas attracted and held Fersman for the rest of his life. After graduation from the University, he had the opportunity to visit different departments of mineralogy in Western Europe and become closely acquainted with many famous scientists. Later he visited many mineral localities of Europe. In 1911 he returned to Petersburg, to the Academy of Sciences, and there began his tireless activity in science and organization which gained for him the reputation of a talented, brilliant scientist.

However, the work in the Academy museum was too confining for the energetic, restless Fersman. During the few years preceding the Revolution, he traveled all over Russia studying ore deposits. It was after the October Revolution, however, that Fersman's talent and knowledge reached full development. These were the romantic years of his creative activity. He did not separate theory from practice. He was fascinated by the unbroken land of the Khibina tundras. The result was the discovery of enormous apatite deposits. The country was presented with the wealth of the Kola Peninsula; and Fersman flew on to the Urals, Siberia and Middle Asia. He organized expeditions and participated in them. One discovery of mineral riches was followed by another. His journeys became legendary. He was acknowledged the foremost authority on the mineral resources and reserves of our country. During long conferences and during journeys, he seized every opportunity to jot down his observations or to write a scientific article. His capacity for work was extraordinary. His papers and books are distinguished not only by the originality and richness of content,

but also by their attractive, easy style. He wrote novelettes and spoke brilliantly. His lectures, reports and impromptu speeches attracted everyone, however complex the subject. His talent as a popularizer was astonishing. Everyone knew this large, massive but mobile man. He surrounded himself with a large group of young and talented scientists. The moving principle of his scientific career was the application of the concepts of physics and chemistry to geologic problems. The first lectures in geochemistry were delivered by Fersman as early as 1912. Together with Vernadskii, he is rightfully considered a pioneer in this new science uniting chemistry and geology. But here also his interests were exceptionally varied. In his four-volume Geochemistry, using his vast experience, he brilliantly discusses biogeochemical and cosmochemical processes. His ideas on the distribution of the elements, their abundance and the laws of their migration will serve many future generations of scientists. His concepts of lattice energy await further development. His regional geochemical studies of the Khibina tundras, Middle Asia, Siberia have not been superseded. The volume on granite pegmatites is a classic. If one recalls his books on geochemical and mineralogical methods of prospecting, on the mineral resources of foreign countries, on gems and decorative stones, the projected series of books on the history of stone and others, one can only be amazed at how much can be accomplished by one man. His contribution to our science, to the discovery and exploitation of the mineral wealth of the Soviet Union, is tremendous. We felt this especially strongly during the time of great trial, World War II. Fersman was deeply concerned and devoted all his strength to helping his native land. He left a vast scientific heritage which all of us use widely and increase with our scientific work. Almost a decade and a half has passed since Alexander Evgen'evich left us. But we, his students, associates and friends cannot forget him. So great is his influence that we feel as if he were still among us today.

A. P. Vinogradov.

# INVESTIGATION OF NEUTRON FLUX IN THE EARTH'S CRUST

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The neutron flux near the earth's surface consists of two components, the cosmic ray secondaries and the neutrons produced by such nuclear processes within the earth's crust as the ( $\alpha$ ,  $n$ ) reactions, spontaneous uranium fission and others. It is the second component that is active within the earth's crust and capable of inducing nuclear transmutations in terrestrial matter. A number of products of such reactions have been investigated--the isotopes of the inert gases of group 0, the transuranium elements, technetium and  $\text{Cl}^{36}$ . On the basis of the content of  $\text{Cl}^{36}$  in uranites, Kuroda and associates [1] established that the neutron flux in a certain area of the earth amounts to  $430 \pm 110 \text{ n/cm}^2 \cdot \text{hr}$ . Direct measurements of neutron flux in the earth's crust were made with thick nuclear emulsions (Eugster [2], Mather [3]). Eugster found a flux amounting to  $0.84 \text{ n/cm}^2 \cdot \text{day}$  in one of the Swiss tunnels, but his results are not free from experimental error. Mather did not find neutron flux exceeding  $0 \text{ n/cm}^2 \cdot \text{day}$  in the deep workings of Australian polymetallic deposits. V.V. Cherdynsev and O.V. Suyarova [7] demonstrated strong neutron flux in the mines of the Akchatau deposit, where the presence of beryllium and radioactive elements favors the generation of neutrons; however, the accuracy of their work was not high.

The neutron flux in the atmosphere produced by cosmic radiation has been adequately studied. A review of the experimental data will be found in reference [4], for example, and of theory, in reference [5]. The neutrons are produced by reaction of the nuclei of atmospheric matter with the particles of cosmic radiation. The flux is at a maximum at the height of about 15 km and decreases towards the earth's surface nearly exponentially. Its intensity near the earth's surface is very small (of the order of  $20-200 \text{ n/cm}^2 \cdot \text{day}$ ) and depends on the altitude and geomagnetic latitude of the place and also on absorption, slowing down and dispersion of the neutrons due to topographic relief and humidity of the near-surface air.

We made rather broad investigations [6], which showed that the neutron flux at different points on the surface of the earth varies, depending entirely on the variation in the intensity of the neutron component of the cosmic ray secondaries due to the above mentioned causes. The terrestrial component of the neutron flux is not detected even in those localities on the earth's surface where increased generation of neutrons might be expected.

(high content of light metals on the surface layer, such as lithium and beryllium, or of radioactive elements). In all investigated cases this component is less than the error of measurement (less than 20% of the neutron flux at the surface). The search for the neutrons of terrestrial origin was made, therefore, in underground mine workings. The present paper is a report of the field investigations of neutron flux in the earth's crust made by us in 1957.

### Method of Measurement

To measure neutron flux we used portable apparatus consisting of tubular proportional counters of the SNM-8 type filled with  $\text{BF}_3$  gas enriched in isotope  $\text{Bi}^{10}$  (up to 88%) and an arrangement for amplification and counting of pulses. It was calculated that the effectiveness of recording of the slow neutrons was about 12%.

Recording of the counting rate,  $n$ , was made by 1) a counter without filters ( $n_1$ ), 2) a counter with a paraffin shield ( $n_2$ ) and 3) a counter with a cadmium absorber of slow neutrons ( $n_3$ ). In the first case the background and the slow neutrons are recorded. In the second, the background and the fast neutrons which passed through the paraffin. In the third, the background, i.e., the pulses produced by the alpha-radiation from the tube walls and the neutrons with energies beyond the thermal energy range which passed through the cadmium filter are recorded.

Combining  $n_1$ ,  $n_2$  and  $n_3$ , it is possible to evaluate the intensity of flux of the slow and fast neutrons. The effect of the fast neutrons is  $n_F = n_2 - kn_1 - (1 - k)n_3$ , of the slow neutrons,  $n_S = n_1 - n_3$ . The sensitivity of the counters to the fast neutrons was measured by a standard polonium-beryllium source. The coefficient  $k$  was determined experimentally and the sensitivity of the counters to the slow neutrons was computed. The formulas for calculating the intensity of flux of the fast and slow neutrons from the counting rates were as follows:

$$I_F = 1.50 n_F \frac{\text{fast neutrons}}{\text{cm}^2 \text{ hour}}$$

$$I_S = 0.54 n_S \frac{\text{slow neutrons}}{\text{cm}^2 \text{ hour}}$$

The sensitivity of the field equipment permitted measurement of neutron flux within  $0.1 \text{ n/cm}^2 \text{ - hour}$ , which is approximately ten times the sensitivity of thick emulsions.

### Results of Measurements

Table 1 presents the results of our measurements made in a number of ore deposits of different types which do not have high content of radioactive elements. In a number of rocks (granodiorites of the Zailiiskii Alatau) and in some hydrothermal deposits (Ak-Kul', Kirghiz SSR; Kvaisa, South Ossetian Autonomous Region, Georgian SSR; Kafan, Armenian SSR) the flux of fast and slow neutrons is extremely small and is less than the error of measurement. The carbonate formations of Kvaisa (barite veins, calcite from the Kudara stalactite cave) have an observable neutron flux ( $I = 0.2 - 0.25 \text{ n/cm}^2 \text{ - hour}$ ).

A weak flux of both slow and fast neutrons was recorded at the molybdenite deposits of Armenia (Kadzharan, Dastakert) and in the granophyres of Kokomeren (Kirghiz SSR) containing a negligible amount of molybdenite. A very weak flux of slow neutrons was detected also in the Tekelii polymetallic deposit.

Much stronger neutron flux was measured in the deposits of rare metals in Central Kazakhstan (Akchatau and Eastern Kounrad). It is related to the early stage of mineralization represented by the development of molybdenite

Table 1

## Measurements of Neutron Flux in Underground Mine Workings

Geological materials	Locality and genesis	Activ- ity in hr/hr.	Flux, $n/cm^2\text{-hour}$	
			slow	fast
Granodiorites	Kazakh SSR, tunnel of Bol'shoi Alma-Ata lake	40	$0.1 \pm 0.2$	$-0.1 \pm 0.1$
Granophyres enriched in molybdenite, Galena-quartz vein	Kirghiz SSR, Narynsk district, Kokomeren	50	$0.6 \pm 0.3$	$1.2 \pm 0.3$
	"	50	$0.5 \pm 0.5$	$0.8 \pm 0.2$
Central Kazakhstan				
Akchatau				
High temperature with molybdenite, beryl and wolframite	Central mine. Early phase of mineralization (enrichment in molybdenite). S.E. mine. Late mineralization (enrichment in beryl)	40-50 up to 400	$2.5 \pm 0.6$ $0.3 \pm 0.3$	$1.8 \pm 0.9$ $0.3 \pm 0.3$
Eastern Kounrad				
	Early albite phase mine No. 7 . . .	30-40	$1.4 \pm 0.3$	$0.5 \pm 0.2$
	mine No. 8 . . .	30-40	$0.9 \pm 0.2$	$0.5 \pm 0.2$
	Late phase (Be, Mo)	30-40	$0.15 \pm 0.25$	$0.4 \pm 0.1$ average of 10 measurements
Armenian SSR				
Hydrothermal copper-molybdenum deposits	Kadzharan	20-30	$0.4 \pm 0.3$ average of 10 measurements	$0.2 \pm 0.1$
	Active points Dastakert	1000 20-30	$0.2 \pm 0.3$ $0.55 \pm 0.15$	$0.9 \pm 0.2$ $0.3 \pm 0.2$ average of 7 measurements
Hydrothermal copper deposit	Kafan	20-30	$0.1 \pm 0.15$	$0.1 \pm 0.1$ average of 7 measurements
Hydrothermal polymetallic deposits	Kazakh SSR, Tekeli	30	$0.4 \pm 0.2$	$0.0 \pm 0.1$ average of 9 measurements
	Kirghiz SSR, Ak-Kul'	30	$0.0 \pm 0.2$	$0.1 \pm 0.2$
Georgian SSR				
Carbonate rocks	Kvaisa	30	$0.0 \pm 0.2$	$0.0 \pm 0.1$
	Kvaisa, barite vein	20	$0.25 \pm 0.2$	$0.2 \pm 0.1$
	Kvaisa, Stalactites, Kudaro cave	20	$0.2 \pm 0.2$	$0.2 \pm 0.1$

in the first locality and of albitized zones in the second. In the zones of early mineralization the slow neutron flux reaches  $I_S = 2.5 \text{ n/cm}^2 \text{ - hour}$  (Akchatau) and  $I_S = 1.4 \text{ n/cm}^2 \text{ - hour}$  (Eastern Kounrad). The fast neutron flux,  $I_F = 1.8$  and  $I_F = 0.5 \text{ n/cm}^2 \text{ - hour}$ , respectively. In the rocks of the later stage of mineralization, the slow neutron flux is within the limit of error and the fast neutron flux is weak ( $0.3 - 0.4 \text{ n/cm}^2 \text{ - hour}$ ) although sometimes these rocks have relatively high activity.

These data confirm the existence of relatively high neutron flux in the central mine of Akchatau (early phase of mineralization) discovered by V. V. Cherdynsev and O. V. Suyarova, but the flux at other points in the same mine, according to our measurements, is tens of times weaker. Unfortunately, the highly radioactive workings investigated by these authors were not accessible during our investigations.

Areas of high radioactivity (southeastern mine of Akchatau; certain points at Kadzharan) do not exhibit substantial increase in neutron flux. Near the veinlets enriched in secondary uranium minerals in the shafts of Kadzharan, the intensity of gamma radiation reaches  $1000 \mu \text{r/hour}$ , but the neutron flux at these points increases by no more than  $\Delta I_F = 1.0 \text{ n/cm}^2 \text{ - hour}$  and  $\Delta I_S = 0.2 \text{ n/cm}^2 \text{ - hour}$ .

Let us review separately the investigation of the neutron flux in the underground workings of the Aktyuz deposit in the Kirghiz SSR (Table 2).

Table 2

Measurements of Neutron Flux in Underground Mining Workings  
at Ak-Tyuz (Kirghiz SSR)

Sample No.	Description of locality	Activity in $\mu\text{r/hour}$	Flux, $\text{n/cm}^2 \text{- hour}$	
			slow	fast
<u>Ak-Tyuz</u>				
1	Horizon No. 4, Shales near mine shaft (country rock)	15	$0.9 \pm 0.5$	$0.0 \pm 0.3$
2	Drift No. 7	100	$2.5 \pm 0.7$	$1.0 \pm 0.5$
3	Apophysa of a vein	400	$4.2 \pm 0.9$	$9.7 \pm 1.7$
4	Horizon No. 5	40	$0.9 \pm 0.7$	$0.0 \pm 0.8$
5	"	100	$1.9 \pm 0.3$	$3.3 \pm 0.6$
6	"	400	$2.5 \pm 0.2$	$7.0 \pm 0.6$
7	"	600	$2.1 \pm 0.3$	$10.7 \pm 0.7$
8	"	700	$3.9 \pm 0.3$	$12.3 \pm 0.9$
9	"	2000	$16.4 \pm 1.4$	$32.4 \pm 1.5$
10	Horizon No. 6, drift 35	500	$7.6 \pm 0.9$	$6.2 \pm 0.7$
11	"	1200	$11.6 \pm 1.6$	$9.4 \pm 1.6$
12	Malyi drift (zone of molybdenite enrichment)	1000	$8.3 \pm 1.6$	$17.4 \pm 1.4$
13	"	1200	$9.7 \pm 1.4$	$21.2 \pm 1.6$
14	"	1200	$13.0 \pm 2.3$	$22.8 \pm 1.7$
15	"	1500	$11.3 \pm 1.4$	$27.7 \pm 2.0$
<u>Kutessai group</u>				
16	Tunnel No. 4	500	$0.6 \pm 0.6$	$12 \pm 1$
17	"	800	$5.8 \pm 0.7$	$7.8 \pm 0.8$
18	Tunnel No. 4	1000	$2.5 \pm 0.6$	$18 \pm 1$
19	"	2000	$24 \pm 2$	$16 \pm 2$
20	Same, drift No. 12	50	$1.3 \pm 0.4$	$0.9 \pm 0.5$
21	Horizon No. 6	600	$8.4 \pm 1.1$	$4.8 \pm 0.8$
22	"	1100	$13.4 \pm 1.6$	$15.0 \pm 1.6$
23	"	1600	$28.2 \pm 1.5$	$26.0 \pm 2.0$

the mineralization there is complex: Its early stage consisted in the introduction of the rare earths and molybdenum accompanied by radioactive elements, while the late hydrothermal stage consisted of enrichment in ad and other metals of the polymetallic complex.

The neutron flux at the Aktyuz deposit is unusually strong. Even at a point with weak gamma-activity (Table 2, No. 20),  $I_S = 1.3$  and  $I_F = 32.4 \text{ cm}^2 - \text{hour}$ .

There is parallelism between gamma-activity and intensity of the fast and slow neutrons. On the average, the increase in neutron flux with increase of  $100 \mu \text{r}/\text{hour}$  in gamma activity is:

$$\Delta I_F \approx 1.8 \text{ and } \Delta I_S \approx 1.1 \text{ n/cm}^2 - \text{hour.}$$

The average  $I_F : I_S$  ratio is nearly 1.6; i.e., it is less than on the earth's surface.

The neutron flux at the Aktyuz deposit is considerably stronger than in other regions with like gamma-activity. It is probable that the flux is related to the  $(\alpha, n)$  reaction between the long range particles of the thorium series with the nuclei of light elements (oxygen-18, fluorine).

The regularities of distribution of neutron flux in the weakly radioactive areas of the earth's crust are only beginning to be outlined, and the data cited here are inadequate to solve the problem. It is possible that some factors in the production of neutrons have not yet been considered.

The value of the  $I_F : I_S$  ratio varies considerably. There are points where the flux consists of slow neutrons only or of fast neutrons only. The precision of determination of this ratio is very low. In some cases  $I_F : I_S = 1.4$  (Kadzharan, points with high activity); in others, it is less than 0.8 (Eastern Kounrad, mine No. 7). Actual variations may evidently exceed this range. In the dry areas of the earth's surface, the  $I_F : I_S$  ratio averages about 20, so that neutron flux of the earth's crust is probably relatively enriched in slow neutrons as compared with the neutron flux near the earth's surface. This may be due to the moisture in the underground workings. In the mines of Eastern Kounrad at especially moist points, the flux of fast neutrons averages  $0.1 \pm 0.2 \text{ n/cm}^2 - \text{hour}$ , i.e., it cannot be measured, while in dry areas it is quite clearly manifested and equals  $0.55 \pm 0.15 \text{ n/cm}^2 - \text{hour}$ . In other regions no definite dependence of the fast neutron flux on the moisture was observed.

Thus, the neutron flux in the weakly active areas of the earth's crust is, on the average, very weak, and the values of  $I_S$  and  $I_F$  do not exceed fractions of a neutron per  $\text{cm}^2 - \text{hour}$ . Only in some ore bodies the neutron flux increases to  $I_S = 2.5$  and  $I_F = 1.8 \text{ n/cm}^2 - \text{hour}$ .

In underground workings with highly radioactive rocks, the neutron flux up to  $I_F = 32.4$  and  $I_S = 28.2$  has been observed. The flux increases on the average by  $\Delta I_F = 1.8$  and  $\Delta I_S = 1.1$  (in neutrons per one  $\text{cm}^2 - \text{hour}$ ) as gamma-activity increases by  $100 \mu \text{r}/\text{hour}$ .

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Received for publication  
June 10, 1958.

## POTASSIUM-ARGON AND LEAD AGES OF SOME GRANITES AND PEGMATITES OF THE MIDDLE DNEPR REGION\*

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The geologic structure of the Middle Dnepr region is very complex and difficult to decipher in detail because of poor exposures. Geophysical data and numerous mine workings and boreholes are of great help.

The dominant structures of the region trend northwest and north-south, and are composed of gneisses, migmatites and schists.

Igneous rocks are widespread and are represented by various granitoids, usually divided into an earlier Kirovograd complex composed mainly of gray granites, and a later Dnepr-Tokovo complex, in which red granites predominate.

Summaries of the geological investigations in the Middle Dnepr region are given in the works of N.P. Semenenko [1, 2], Yu. Ir. Polovinkina [3], N. Kotlyar [4], A.P. Nikol'skii [5] and a number of other authors.

At present there is only a preliminary structural-lithological map of the Middle Dnepr region (N.P. Semenenko and others, 1957).

Extensive use of the methods of absolute geochronology made it possible to introduce significant corrections into our concepts of the Precambrian history of the Ukraine.

Some age data for the Middle Dnepr region, obtained in a number of laboratories, have already been published (E.K. Gerling [6], L.V. Komlev [7], N.I. Polevaya [8]).

In the present paper we are using new data obtained by the potassium-argon method on micas separated from some of the granites and pegmatites of the Middle Dnepr region and by the isotopic lead methods on the accessory monazites and allanites from pegmatite dikes.

\* Read at the VII session of the Committee for Determination of the Absolute Age of Geologic Formations.

Table 1

## Argon Ages of Micas from Granodiorites, Plagioclase-rich Granites and Granites of the Middle Dnepr Region

Sample No.	Locality	Type of Rock	Content, %			Age, $10^6$ years	
			K	$A \cdot 10^{-4}$	$A^{40}/K^{40}$	$\lambda_e = 0.6 \cdot 10^{-10}$	$\lambda_e = 0.557 \cdot 10^{-10}$
191/55	Yamburg quarry, Mokraya Sura River	Biotite from pegmatite veinlets in granodiorite	6.14	2.81	0.382	2710	2900
		Biotite from granodiorite with an admixture of amphibole	3.19	1.49	0.389	2720	2910
		Biotite from the Saksagan' plagioclase-rich granites	5.74	1.56	0.226	2020	2170
190/55	Quarry near Temnovaty Kut on the Saksagan' River	Biotite from rose-gray Kremenchug granodiorite	5.16	1.38	0.223	2000	2150
		Biotite from gray granodiorite	5.14	1.13	0.183	1770	1900
		Hornblende-biotite fraction from gray coarse-grained porphyritic granodiorite	2.82	0.60	0.176	1730	1860
1419	Kryukovo quarry MPC near Kremenchug	Chikalov quarry No. 3, below Kremenchug					
226/55							
229/55							
227/55							

Argon Ages of Micas from Granodiorites, Plagioclase-rich Granites and Granites of the Middle Dnepr Region

Sample No.	Locality	Type of Rock	Content, %			Age, 10 <sup>6</sup> years	
			K	A · 10 <sup>-4</sup>	A <sup>40</sup> /K <sup>40</sup>	$\lambda_e = 0.6 \cdot 10^{-10}$	$\lambda_e = 0.557 \cdot 10^{-10}$
389/48	Domotkan'sk quarry above Verkhne-Dneprovsk	Biotite from gray medium-grained granite	5.36	1.42	0.213	1950	2100
201/55	Korbino quarry below Verkhne-Dneprovsk	Biotite from pegmatite in migmatite	5.57	1.64	0.245	2130	2280
266/47	Village of Shevchenko on the Berezova River, Dolinsk massif	Biotite from coarse-grained gray porphyritic granite of Kirovograd type	5.83	1.49	0.213	1950	2100
163/55	Novo-Danilovsk quarry	Biotite from red coarse-grained porphyritic granite	6.51	1.57	0.201	1880	2020
164/55	Same	Biotite from pegmatite in red coarse-grained porphyritic granite	6.21	1.44	0.193	1830	1970
496/48	Yantsev quarry, Zaporozh'e	Biotite fraction from typical medium-grained gray granite	4.32	1.00	0.188	1810	1940

Table 1 (Cont'd.)

Argon Ages of Micas from Granodiorites, Plagioclase-rich Granites and Granites of the Middle Dnepr Region

Sample No.	Locality	Type of Rock	Content, %			Age, 10 <sup>6</sup> years		
			K	A · 10 <sup>-4</sup>	A <sup>40</sup> /K <sup>40</sup>	$\lambda_e = 0.6 \cdot 10^{-10}$	$\lambda_e = 0.557 \cdot 10^{-10}$	$\lambda_\beta = 4.90 \cdot 10^{-10}$
172/52	Same	Biotite from gray medium-grained granite Biotite from red coarse-grained granite enriched in biotite; mixed sample	5.71	1.41	0.206	1910	2050	
360/48	Tokovo quarries	Biotite from red contaminated granite Gray coarse-grained granite Rock sample	6.20	1.28	0.1720	1700	1830	
169/55	Podstepnoe quarry		6.55	1.47	0.1870	1800	1930	
425/53	Tokovo quarry near waterfall on the Kamenka River		4.43	0.87	0.164	1650	1770	

The results of age determinations are presented in the tables.

Let us consider briefly the results of the potassium-argon method (Table 1) computed on the basis of the new decay constants of  $K^{40}$  proposed by American authors (Wetherill et al. [9]).

These constants,  $\lambda_e = 0.557 \cdot 10^{-10}/\text{yr}$ ,  $\lambda_\beta = 4.72 \cdot 10^{-10}/\text{yr}$ , must be considered as more exact than the older ones.

For comparison the table gives also the figures obtained with the old constants of E. K. Gerling [10],  $\lambda_e = 0.60 \cdot 10^{-10}/\text{yr}$  and  $\lambda_\beta = 4.9 \cdot 10^{-10}/\text{yr}$ , which until now have been used in age determinations in the Soviet Union.

The new decay constants of  $K^{40}$  give K-A ages higher by 7 to 8%, and this brings the results of the argon method closer to those obtained by the isotopic lead methods.

In Table 1, attention is attracted by the unusually high age of 2900 million years obtained for biotite from a pegmatite cutting granodiorite of the Yamburg quarry on the Mokraya Sura River.

This figure was obtained twice. It has been checked on the biotite-amphibole fraction separated from the granodiorite itself, which gave the age of 2910 million years.

At present this is the highest age obtained by the K-A method for the Precambrian of the Ukraine.

The ages obtained for the plagioclase-rich granites of the Saksagan' River (quarry near the village of Ternovatyi Kut) and the Kremenchug granodiorites (Kryukov and Chikalov quarries) range from 1900 to 2700 million years and agree well with the earlier data obtained by Gerling [6] and N. I. Polevaya [8], which, when recalculated with the new constants, give 2100 million years.

The age of 1860 million years was obtained for the Taburishchensk porphyritic granodiorites. They are usually considered a part of the Korovograd igneous complex.

The biotite from the gray medium-grained granite of the Comotkansk quarries on the Dnepr River gave a very high age of 2100 million years, which contradicts the idea that these granites belong to the Dnepr-Takovo complex. A still higher age, of 2280 million years, was obtained for the biotite from a pegmatite cutting the migmatites at the Korbino quarry.

Allanite separated from the same pegmatite gave ages of the same order of magnitude—2100–2610 million years for all isotopic ratios (Tables 2 and 4).

Thus, the very high ages of the Korbino pegmatites have been established by two independent methods. Evidently the Korbino and Domotkani granites are much older than was generally believed until now.

For the Dolino massif of coarse-grained porphyritic granites, the age of 2100 million years was measured on biotite separated from the typical gray granite of the Shevchenkovo quarry on the Berezovaya River.

Similar values, of 1970 to 2020 million years, were obtained for biotite from the red coarse-grained porphyritic granite and the associated pegmatites of the Novo-Danilovsk quarry. Two samples of monazite were separated from the same red porphyritic granite, whose ages could be calculated on the basis of thorium lead only, because of their low uranium content in monazite.

The age of 2100 million years obtained for both samples confirms the correctness of other determinations (Tables 2–4).

As is well known, Yu. Ir. Polovinkina [3] proposed that the red Novo-Danilovsk granite be considered as genetically related to the "black"

Table 2

Radiochemical Data for Monazites and Allanites  
of the Middle Dnepr Region

Sample No.	Locality and type of rock	Content, %		
		Th	U	Pb
165/55	Novo-Danilovsk quarry. Monazite from red porphyritic granite	5.24	0.066	0.555
165/55 - A	Same	4.26	0.054	0.46
1408*	Korbino quarry. Allanite from pegmatite cutting migmatites	1.50	0.046	0.190
436/53*	Staryi Podstepenskii quarry. Allanite from pegmatite of the marginal zone of Tokovsk massif	0.78	0.026	0.114

\* All analyses were performed twice. In each case 2-3 parallel determinations were made.

Table 3

## Isotopic Composition of Lead in Monazites and Allanites

Sample No.	Locality	Lead isotopes				Admixture of ordinary lead, %
		204	206	207	208	
165/55	Novo-Danilovsk quarry (monazite)	0.073	4.04	0.90	100	4.5
165/55-A	Same	0.108	4.48	1.14	100	6.6
1400	Korbino (allanite)	0.069	9.88	2.51	100	3.96
436/53	Podstepnoe (allanite)	0.119	15.60	4.07	100	6.4

Bokovyansk quartz granite, which, according to our determinations, is much younger (Komlev et al. [11]).

Ages ranging from 1940 to 2050 million years were measured on biotite from two samples of typical gray medium-grained Yantsevo granite of Zaporozh'e, which therefore can be referred to the Kirovograd complex.

Of considerable interest are the ages obtained for the well-known red thorite-bearing Tokovo granite which forms a large pluton in the lower courses of the Bazavluk and Kamenka rivers.

After unsuccessful attempts to obtain pure biotite from powdered normal Tokovo granite, we decided to use samples of granite enriched in

Table 4

Ages of Minazites and Allanites of the Middle Dnepr Region

Sample No.	Locality	Ages, $10^6$ years				
		$\Sigma \text{Pb}$ U + Th	208 Th	206 U	207 U	207 206
165/55	Novo Danilovsk quarry (monazite)	2050	2100	1580	-	-
165/55-A	Same	2040	2100	1520	-	-
1408	Korbino quarry (allanite)	2320	2320	2100	2350	2610
436/53	Staryi Podstepenskii quarry (allanite)	2550	2400	3000	2720	2560

biotite by assimilation of small xenoliths of basic rocks (amphibolites). We regarded this biotite as the product of assimilation, for it is highly improbable that relict biotite from the amphibolites could have been preserved. Two samples of biotite from the contaminated portions of granite gave ages of 1830 and 1930 million years.

An analysis of Tokovo granite made on a sample of the typical gray coarse-grained rock from the quarry near the waterfall on the Kamenka river gave the age of 1770 million years.

It may be considered, therefore, that the age of the Tokovo granite is between 1770 and 1930 million years.

A quite unexpected result was obtained from allanite from the pegmatitic segregations in the old Podstepensk quarry.

The quarry is located at the extreme zone of the eastern contact of the Tokovo pluton and reveals a large area of intensively granitized country rock with numerous aplite-pegmatite bodies. The rocks are very variable in structure, composition and color. Side by side with the grayish-red granite there are various hybrid rocks enriched in white plagioclase and amphibole. There are also numerous inclusions of gneiss in the granites in the form of separate thin layers and xenoliths.

The pegmatites are thin steeply dipping dikes of quartz-feldspathic composition. But there are also irregular nest-like segregations of quartz and feldspar with sparse black crystals of very fresh allanite. The sample of allanite for age determination was collected from several pegmatites of the same type.

The thorium and uranium content in allanite is low -- 0.78% Th and 0.26% U -- and this appeared strange in light of the assumed genetic relationship between the allanite and the Tokovo granites strongly enriched in thorium.

Calculations of the isotopic lead ages gave very high values for all isotope ratios, ranging from 2400 to 3000 million years, and a satisfactory agreement between individual values (Tables 2-4). The admixture of common lead amounts to 6.4%.

The results of age determinations on the Podstepensk allanite may be interpreted only on the assumption of the relict nature of the allanite

pegmatites, possibly related genetically not to the Tokovo granites but to the older aplite-pegmatite facies responsible for the widespread migmatization of the Dnepr region gneisses.

Thus, allanite from the old Podstepensk quarry is quite analogous to the allanite from the migmatites of Ingul'ts and Saksagani, for which A. P. Vinogradov and A. I. Tugarinov [12] obtained equally high ages.

The relict character assumed for the allanite pegmatites explains well the low thorium content in the allanite.

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# ON THE GEOCHEMISTRY OF LEAD IN THE DEVONIAN EXTRUSIVES OF CENTRAL KAZAKHSTAN

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The problem of the behavior of minor elements during petrogenesis cannot be solved without the knowledge of their distribution in extrusive as well as intrusive rocks.

Of the numerous investigations of the geochemistry of igneous rocks made during recent years, only a few are devoted to extrusive rocks [1-6] or consider them to some degree.

These investigations were made on volcanic series well known geologically and analyze the behavior of a large number of minor and dispersed elements (including lead) during the process of differentiation. But in only three of these studies [1, 2, 4] were quantitative methods of determination used.

These few investigations indicate that genetically related series of rocks in North America, Polynesia and other regions show a tendency towards relative enrichment of the late acid derivatives in lead. In the calc-alkalic series this tendency is more evident and definite than in the alkalic series. This is known to be true also of intrusive complexes.

## Brief Account of the Geology and Petrography of the Devonian Extrusives of Central Kazakhstan

Investigation of the geochemistry of lead in the extrusives of Central Kazakhstan is not only of theoretical but of practical interest. There are several polymetallic lead deposits and occurrences in this region, not older than the Famennian-Tournaisian age, which are regarded as sedimentary in origin by some geologists, and the Devonian extrusives covering large areas in Central Kazakhstan are believed to be the main source of lead in these deposits.

The material for the present work was collected in the following regions of Central Kazakhstan: Mt. Terekta (M-42-XXXIII), Mt. Kuzhal (M-42-113), Mt. Munglu (L-42-V) and along the course of the Kara-Sai River (L-42-VI).

The first two localities are in the western part of Central Kazakhstan, 100 km to the northeast of Dzhezkazgan, and are geologically related to the Sarys-Teniz uplift. The next two are in the northern part of Bet-Pak-Dala. It should be mentioned that no systematic sampling was done in the Devonian section of the Mt. Kuzhal region, but several samples of rhyolitic tuffs were taken from the Lower-Middle Devonian sequence.

The Devonian system in the enumerated regions, as well as in Central Kazakhstan as a whole, consists of three main stratigraphic units: 2) the undifferentiated volcanic rocks of the Lower and Middle Devonian  $D_{1-2}$ , b) the volcanic and sedimentary Zhaksykon series, referred to the upper part of the Middle Devonian and the base of the Upper Devonian, including the

Frasnian stage,  $D_2$ - $D_3$ <sup>fr</sup>, and c) the Upper Devonian carbonate beds of the Famennian stage,  $D_3$ <sup>fm</sup>.

In the Devonian section, only the Lower-Middle Devonian extrusive rocks of the lower Zhaksykon volcanic series were sampled and studied. The  $D_{1-2}$  deposits in the lower part of the section are composed of andesitic and dacitic extrusives, mainly lava flows. In the upper part of the section, rhyolitic pyroclasts are predominant. The extrusives of the Zhaksykon formation are characterized by a) frequent facies changes (along the strike and vertically), b) the presence of amygdaloidal varieties of andesites and dacites, and c) the presence of numerous bed of clastic rocks.

Among the extrusives of the regions under investigation, three main groups may be separated: andesitic, dacitic and rhyolitic. It has already been mentioned that in the first two groups lavas are predominant, but the acid extrusives are mainly pyroclasts (tuffs).

Microscopic study shows that the lavas have a variety of porphyritic textures and aphyric rocks are rare. The phenocrysts in the andesites and dacites are plagioclase ( $An_{40}$ - $An_{50}$ ), hornblende and pyroxene (augite and hypersthene). In the dacites, albite is dominant among the phenocrysts and the dark minerals and quartz are subordinate. The groundmass in these rocks contains relicts of hyalopilitic and intersertal textures. In the acid rocks (rhyolites and quartz albitophyres) the phenocrysts are quartz, feldspars in various proportions (sanidine and albite) and biotite. The groundmass of the acid lavas is usually felsitic. Zircon and apatite are notable in these lavas among the accessory minerals.

The rhyolitic tuffs consist of fragments of quartz, feldspars and biotite in a matrix composed of shards of glass. The glass is devitrified into felsite. In the region of Mt. Terekta, only tuffs are found, but along the course of the Kra-Sau River there are rhyolitic ignimbrites with the characteristic pseudo-fluidal structure of the groundmass.

As a result of alteration, the dark minerals of the extrusives have been rendered opaque and chloritized, the feldspars have been sericitized and saussuritized, and secondary quartz, carbonate and fine-grained albite were formed. Thus, the alteration may be referred to the lowest rank of regional metamorphism, the greenschist facies. The nature of albite phenocrysts in the dacites (albitophyres) is not clear.

In the selection of samples special effort was made to collect fresh specimens representative of the given type of rock. The weight of the samples before they were powdered was 200-250 g. Average samples were made by mixing equal weights of material representing a given rock type.

Methods of Lead Determination

Spectrography was the basic method used in lead determination. We utilized the technique developed for analysis of zircon [7].

The persistent 2833.07 Å lead line was used. The standards were prepared with a quartz base, and lead was introduced in the form of  $Pb(NO_3)_2$  solution. Both the samples and the standards were mixed with  $Na_2CO_3$  in 1 : 3 ratio. The 2897.97 Å bismuth line served as the internal standard. Bismuth was introduced into soda in the form of  $Bi_2O_3$  to bring the Bi content to 0.005%.

The sample, weighing 50 mg, was placed in the cavity drilled in the cathode and measuring 4 mm in diameter and 7 mm in depth. A d.c. arc with 4 mm gap operated at  $I = 12.5$  amps served as the light source. The analyses were made on the quartz spectrograph ISP-28 with 6  $\mu$  slit; the spectra were photographed on spectroscopic plates of type 2.

Lead and bismuth evaporation curves obtained from samples and standards containing  $Na_2CO_3$  buffer were studied. The possible variation in the relative intensity of lead and bismuth lines due to slight differences in their excitation potentials and the differences in the total composition of the samples and the base of the standards were calculated. These data proved the applicability of the technique to the determination of lead in silicate rocks. The average reproducibility of the results was  $\pm 8\%$ . Analyses of control samples were kindly made for us by L.I. Pavlenko, Associate of the Vernadskii Institute of Geochemistry and Analytical Chemistry. A comparison of spectrographic determinations with those made by the dithizone method for several samples (Table 1) without the use of a radioactive tracer shows that the accuracy of the spectrographic method is  $\pm 15\%$ . Its limit of detection is  $0.2 \cdot 10^{-3}\%$ .

Table 1

Comparison of Results of Lead Determination  
(Pb content in %)

Sample	Method	Spectro-	Chemical	Spectrographic (L.I.-Pavlenko, Inst. Geokh. & Anal. Chem.)	Chemical (L.V. Tauson, Inst. Geokh. & Anal. Chem.)
		graphic	(different investigators)		
257		$1.5 \cdot 10^{-3}$	-	$1.5 \cdot 10^{-3}$	$1.7 \cdot 10^{-3}$
258-a		$1.4 \cdot 10^{-3}$	-	$1.3 \cdot 10^{-3}$	$1.3 \cdot 10^{-3}$
5-K		$3.0 \cdot 10^{-3}$	-	$2.3 \cdot 10^{-3}$	$2.0 \cdot 10^{-3}$
Dacite tuffs, average sample		$2.6 \cdot 10^{-3}$	$2.3 \cdot 10^{-3}$	-	-
409/1039		$1.5 \cdot 10^{-3}$	$0.9 \cdot 10^{-3}$	-	-
452/1120		$1.4 \cdot 10^{-3}$	$1.3 \cdot 10^{-3}$	-	-
294/858		$1.2 \cdot 10^{-3}$	$1.5 \cdot 10^{-3}$	-	-
372/972		$1.5 \cdot 10^{-3}$	$1.4 \cdot 10^{-3}$	-	-

Table 2  
Blood Content in the Extrusives of Some Regions of Central Kazakhstan

### Discussion of Results

The results of our lead determinations are presented in Table 2.

The published data on the lead content in the intermediate extrusive rocks are very scant and contradictory. This makes it difficult to compare our data with the clarkes. According to Amstutz [1], the lead content in the Carboniferous-Permian spilites of Switzerland ranges from  $2.8 \cdot 10^{-4}$  to  $1.5 \cdot 10^{-3}\%$ . That lead is concentrated in the acid members of genetically related groups of rocks is well established for volcanic series and intrusive complexes which have been thoroughly investigated geologically. Thus, the volcanic series of the Clear Lake region (California) changes in composition from olivine basalt through the intermediate andesite and dacite to rhyolitic obsidian. The  $\text{SiO}_2$  content in the series increases from 56% to 76% and the lead content from  $0.8 \cdot 10^{-4}$  to  $2.0 \cdot 10^{-3}\%$ . The volcanic series of Lassen Peak, central Sierra Nevada, and the alkalic series of Polynesia, Hawaii and some other islands [1-6], show a similar distribution of lead.

Such examples are more numerous for intrusive complexes, for example, for the Susamyr intrusives studied by L. V. Tauson [8, 9] and for other complexes, in all of which granitic dike facies have the highest lead content.

Our results are discussed in reference to three groups of extrusive rocks: andesitic, dacitic and rhyolitic.

In the study of the primary lead content, we used lavas, in which the probability of secondary enrichment (see below) is considerably less than in tuffs, and the lead content may be considered identical with the primary content in magma.

Table 3 presents the computed average lead content.

For the acid lavas (rhyolites and quartz albitophyres) lead content is almost half of the average lead content in the acid igneous rocks of the earth's crust (Tables 3 and 4).

Table 3

Average Lead Content in the Extrusives of Central Kazakhstan

Rock	Region		Mt. Terekta		Kara-Sai River		Mt. Munglu	
	10 <sup>-3</sup> %	Number of samples						
Rhyolites, quartz albitophyres	1.3	3	1.0	7	-	-	-	-
Dacites	1.1	12*	1.2	2	0.8	7		
Andesites	1.8	10*	0.5	2	0.4	4		
Rhyolite and quartz albitophyre tuffs	2.0	10	1.4	9	1.3	9		
Dacite tuffs	2.5	3*	-	-	-	-		

\* Analysis of an average sample of the given number of samples

Table 4

Average Lead Content in the Igneous Rocks  
of the Earth's Crust, %

Rock	Author	
	A. P. Vinogradov, 1956 [10]	K. H. Wedepohl, 1956 [11]
Granites (rhyolites, obsidians)	$2.0 \cdot 10^{-3}$	$2.0 \cdot 10^{-3}$
Granodiorites (rhyo-dacites)	-	$1.5 \cdot 10^{-3}$
Quartz diorites, tonalites (dacites)	-	$1.0 \cdot 10^{-3}$
Diorites, monzonites (andesites)	$1.5 \cdot 10^{-3}$	$1.0 \cdot 10^{-3}$
Gabbros (basalts)	$8.0 \cdot 10^{-4}$	$6.0 \cdot 10^{-4}$
Ultrabasic rocks	-	$3.0 \cdot 10^{-4}$

The lead content in dacites and andesites varies from one region to another by a factor ranging from 2 to 4. The acid lavas are characterized by a more uniform distribution of lead, both in individual sections and in Devonian sections located at considerable distances from each other. In the sections on the Kara-Sai River and on Mt. Terekta the acid varieties of the andesite-dacite-rhyolite series are not noticeably enriched in lead. It may even be said that in the Mt. Terekta section the opposite tendency is observed. Unfortunately, there are no data on the lead content in Devonian granites. For two dikes of leucocratic granite porphyry cutting the Devonian volcanic series at Mt. Monglu, low values were obtained for lead content:  $0.6 \cdot 10^{-3}$  and  $0.4 \cdot 10^{-3}\%$ .

As was to be expected, the addition of radiogenic lead, computed for four samples (Nos. 1, 9, 12 and 17, Table 2), in which the U and Th content was determined by radioactivity, is negligible and amounts to only 2-2.5% of the total lead content.

It is evident that lead content does not depend on the composition of the extrusive. There is no unique explanation for this fact. It may be due to the absence of genetic relationship or the peculiarities of evolution of the magmatic chamber, or it may be due to some still unknown factors.

The average lead content in rhyolitic and quartz albitophyre tuffs, according to all available data, is  $1.3 \cdot 10^{-3}\%$  and in lavas of the same composition,  $1.0 \cdot 10^{-3}\%$ . In the region of Mt. Terekta, the tendency towards enrichment of the tuffs in lead is stronger than in all other investigated regions. The average lead content in the acid tuffs and lavas in this region is  $2.0 \cdot 10^{-3}$  and  $1.3 \cdot 10^{-3}\%$ , respectively. Approximately the same relation is shown by the average samples for dacitic tuffs and lavas:  $2.5 \cdot 10^{-3}$  and  $1.1 \cdot 10^{-3}$ , respectively.

Using 42 values for the lead content in rhyolitic tuffs and 14 values for its content in rhyolites, we plotted frequency distribution curves for lead concentration (Figs. 1 and 2), using the concentration and the number of samples having lead content within a given interval of concentration as the two variables. For easier comparison, each axis in the two graphs is divided into equal intervals. The horizontal axis is divided into equal intervals

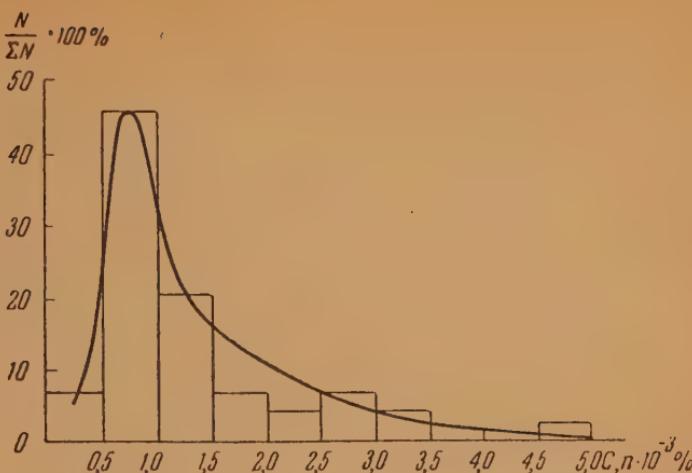


Fig. 1. Frequency of distribution of lead concentration in rhyolite tuffs

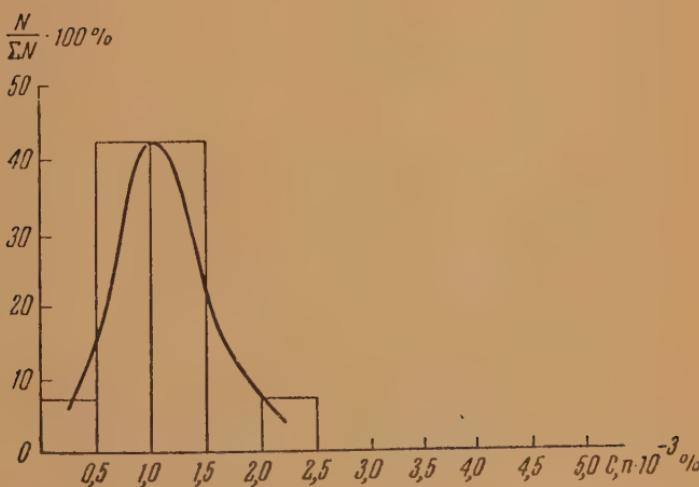


Fig. 2. Frequency of distribution of lead concentration in rhyolites

of lead concentration-- $0.5 \cdot 10^{-3}\%$ , which exceeds the probable absolute error of determination. The number of samples falling into a given concentration interval and expressed in percent of all samples ( $\frac{N}{\Sigma N} \cdot 100\%$ ) is plotted on the horizontal axis. In other words, the graphs are normal curves.

An examination of the graphs shows that in both of them the maximum number of samples (65% of tuffs and 85% of lavas) have lead content ranging

from  $0.5 \cdot 10^{-3}$  to  $1.5 \cdot 10^{-3}\%$ .

Only 28% of all tuff samples and 7% of lava samples have lead content higher than  $1.5 \cdot 10^{-3}\%$ . The upper limit of lead concentration in the lavas is  $2.2 \cdot 10^{-3}\%$ , while in the tuffs it is  $5.0 \cdot 10^{-3}\%$ . Thus, relatively few tuff samples (~20%) are enriched in lead, but this gives the average tuff samples a higher lead concentration than that in the lavas.

Two theoretical explanations of the enrichment of tuffs in lead are possible: a) it is a primary (magmatic) feature or b) it is the result of epigenetic processes.

Primary enrichment of tuffs in lead as compared with the associated lavas of identical composition is improbable because it could be due only to the difference in the mechanics of formation of tuffs and lavas, for all other conditions (magmatic source, composition and age) may be considered identical.

The difference in the mechanism of formation of lavas and pyroclasts is merely in the mode of extrusion of magma, flow in the case of lavas, ejection in the case of tuffs. These two processes are intimately related, often alternate and result in the formation of "tuff-lavas." It is improbable that the difference in the extrusion of magma from the magmatic chamber could affect the distribution of the elements in it, especially as either process, flow or ejection, is of very short duration.

It is more probable that the unconsolidated, porous structure of freshly deposited ash favors the circulation of solutions condensed from volcanic emanations, of fumarole liquids and surface waters.

This process is likely to have only a local effect and not affect the entire rock mass, and this is precisely what is actually observed. The introduced lead exists apparently in a different, more mobile form in fractures, interstices, etc., than the primary lead. It must be borne in mind, however, that, in the process of alteration of tuffs, part of the introduced lead may pass into the form in which it is usually found in igneous rocks (diamictic substitute, sulfide).

Moreover, the possibility is not excluded of a still later hydrothermal process, also leading to local enrichment in lead.

The following considerations suggest, in our opinion, that the anomalous lead content is of secondary origin.

Ahrens [12] has shown on the basis of about one thousand determinations of twenty minor and dispersed elements in the igneous rocks of Canada that the logarithm of concentration of an element in a particular igneous rock has normal distribution. R. Miller and E. Golberg [13] reviewed Ahrens' data mathematically and came to the conclusion that the logarithmically-normal distribution of an element for any interval of the logarithm of distribution holds true for only six elements, including Pb, Cr, V and others.

The logarithmically-normal distribution of the elements in igneous rocks is characteristic, evidently, of the primary content; i.e., it is determined by the content of an element in the magma.

That there is no normal distribution of lead in tuffs is shown by the frequency distribution curve (with the logarithm of concentration as one of the variables) (Fig. 3). The curve indicates a strong positive deviation. This suggests that, besides the magmatic lead, the tuffs contain a certain amount of introduced lead, which changes the pattern of the logarithmic-normal distribution. The hypothesis of possible introduction of elements, and of lead in particular, is further confirmed by the interesting observation

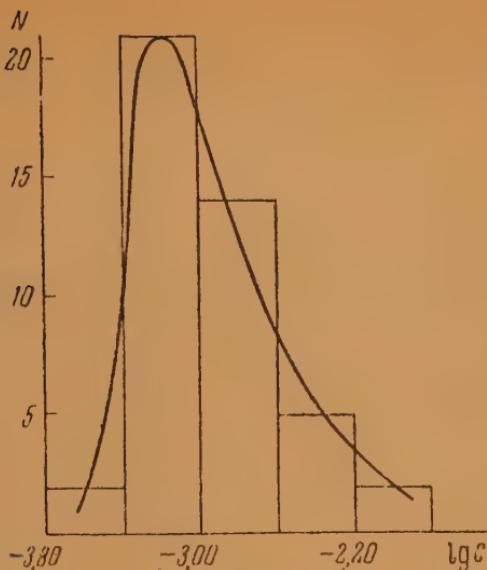


Fig. 3. Frequency of distribution of logarithm of lead concentration in rhyolite tuffs

of E. I. Tikhomirova\* that barite and fluorite occur rather often in the tuffs of the Sarys-Teniz uplift but are absent from the lavas.

There is no regular change in the lead content vertically in the section in the similar kinds of rocks. But certain regional differences should be mentioned. In the Mt. Terekta region the lead content is relatively higher in almost all types of rocks than in other regions. No special study of the behavior of lead in the altered extrusives was made. Five available determinations (Table 2) show that there is no noticeable difference in this respect between silicified and unaltered rocks.

The authors express their gratitude to L. I. Blokhina, M. A. Petrova, N. I. Stupnikova and L. A. Borisenok for their help in this research.

#### Summary

1. The lead content in the Devonian extrusives of the investigated regions of Central Kazakhstan is lower than the clarkes for the igneous rocks of the corresponding types.
2. There is no observable enrichment in lead of the acid varieties of rocks.

\* Oral communication.

3. The slightly higher lead content in the extrusives of Mt. Terekta suggests regional variation.

4. Some samples of rhyolitic tuffs are enriched in lead as compared with the samples of lavas of equivalent composition. This enrichment is most likely secondary.

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Received for publication  
June 26, 1958.

## THE Hf/Zr RATIO IN ZIRCONES FROM GRANITE PEGMATITES

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It was shown in previous investigations that the Hf/Zr ratio in intrusive rocks changes regularly during the process of their formation and may be used as a characteristic indicator of the conditions of emplacement [1-6]. The present work is a continuation of these studies. It is devoted to the determination of the behavior of zirconium and hafnium during the pegmatic process connected with granitic magmas.

With this object in mind, a study was made of the zircon group minerals from different granite pegmatites.

It should be mentioned that typical zircons are not characteristic of granite pegmatites; they occur only in the contact areas and among the assimilated zenoliths of the enclosing rocks and, as in granites, they are found usually as inclusions in biotite. On the other hand, such members of the zircon group as cyrtolite and malacon are very characteristic of pegmatites and are of considerable interest. In the literature, very similar minerals of the zircon group from different localities are often described under different names, and at present the following varieties occurring in pegmatites must be considered as members of this group: cyrtolite, malacon, alvite, naegite, hagatalite, oyamalite, yamaguchilite, and högtveitite.

These minerals differ from typical zircon in a number of characteristics which unite them into a perfectly definite group. Among these are the following:

a) All minerals of this group contain from 1.5 - 2 to 12% of water. It was shown by E. E. Kostyleva [7] that most of the water is liberated between 200 and 250°C.

b) All minerals of this group have relatively high uranium and thorium content. In the albitized pegmatites with rare metals these minerals are the main concentrators of uranium. The form in which uranium and thorium occur in them is varied (from minute mechanical inclusions of

uraninite and thorite to diadochic replacement in the mineral lattices) and is still insufficiently known.

c) A characteristic feature of these minerals is the presence of yttrium earths in amounts up to 8-10%. The cyrtolites with rare earths are always enriched in phosphorus (yamaguchilite, oyamalite), niobium (naegite), and arsenic. In some cases their high content of rare earths is due to the presence of minute inclusions of xenotime or fergusonite (epitaxic intergrowths).

d) The minerals of the cyrtolite-malacon type are largely metamict and are characterized by anomalous crystal form (deformed and twisted crystals with convex faces, platy aggregates); they have a much lower specific gravity and are softer ( $H = 6 - 6.5$  instead of 7-8) than zircon.

e) It will be shown below that these varieties of zircon have the highest hafnium content of all known minerals, as high as 10-14% in some cases, and may be regarded as hafnium minerals.

It should be pointed out that the cyrtolites of the pegmatites with rare metals crystallize out at different stages of the pegmatitic process and occur in pegmatite bodies of different types. According to the time of crystallization, morphological characteristics and paragenetic association, several varieties of the zircon group of minerals may be distinguished.

#### Zircons in Medium-Grained and Coarse-Grained Plagioclase-Microcline-Biotite Pegmatites

In the peripheral zones of the plagioclase-microcline pegmatites there are sometimes small elongated zircon crystals entirely enclosed in biotite or feldspar. In their crystal habit they differ little from the typical accessory zircons of granites.

When the composition of the pegmatite approaches that of syenite, or when it is genetically related to quartz syenite or syenite, the zircon crystals become larger and much more numerous. Such, for example, are the large reddish-brown zircon crystals typical of the pegmatites of the Il'men' Mountains and some other regions. It should be pointed out that the  $HfO_2$  content in these zircons is somewhat lower than in the zircons from normal granites and is very characteristic of alkalic granites (Table 1, analyses 1-7).

#### Typical Cyrtolites of Plagioclase-Microcline Pegmatites with Uranium and Rare Earths

According to the data of A. N. Labuntsov [8], the plagioclase-microcline pegmatites rich in rare earth minerals (Type II in Fersman's classification), besides the small elongated zircon crystals, often contain stubby, flattened cyrtolite crystals with deformed and strongly convex faces. These cyrtolites are always found in regular intergrowth with xenotime. They occur most often between flakes of biotite, less commonly of muscovite, and are very intimately associated with xenotime, allanite, uraninite, metamict tantal-niobates, and sometimes with garnet. The uraninite often occurs as minute inclusions in cyrtolite and sometimes is completely altered to gummite. Cyrtolites of this kind are characteristic of the pegmatites of Northern Karelia, Southern Norway, Sweden, and Canada.

Table 1

ZrO<sub>2</sub> and HfO<sub>2</sub> Content in Minerals of the Zircon Group

Specimen No.	Locality	ZrO <sub>2</sub>	HfO <sub>2</sub>	ZrO <sub>2</sub> /HfO <sub>2</sub>
Zircons from coarsely-crystalline biotite-microcline pegmatites				
1	Czechoslovakia, Bohemia	64.5	0.72	89
2	The Urals, Il'men' Mts.	65.2	1.19	55
3	same	65.0	1.41	46
4	"	65.0	1.20	54
5	"	63.0	1.20	52
6	"	63.9	1.05	61
7	"	66.0	1.01	60
Average for Il'men Mountains				54.7
Cyrtolites from Uranium - Rare Earths Pegmatites				
8	Northern Karelia	44.4	2.68	16.5
9	"	52.0	4.00	13.0
10	"	55.6	6.12	9.1
11	"	54.0	3.8	14.2
12	"	63.0	3.45	18.2
13	Norway, Hitero"	63.0	3.00	21.0
Average				15.3
Cyrtolite from Beryllium - Muscovite Pegmatites				
14	Turkestan Range	57.9	3.35	17.3
Cyrtolites from Albitized Pegmatites				
15	Kolbinskii Range	61.0	5.30	11.5
16	"	61.0	5.30	11.5
17	"	59.0	7.40	8.0
18	Canada	61.0	6.30	9.7
Average				10.2
Late Cyrtolites from Replacement Pegmatites				
19	Kolbinskii Range (cyrtolite)	53.0	10.0	5.3
20	Ukrainian SSR (cyrtolite)	51.0	13.8	3.7
21	same	56.0	10.4	5.4
22	Norway, Tangen, (alvite)	58.0	9.2	6.3
23	Norway, Kragero, (alvite)	60.0	6.6	9.1
24	Japan, Naego (naegite)	60.0	10.0	6.0
Average				6.0

Analyses show that they have a relatively high  $\text{HfO}_2$  content and hence their  $\text{ZrO}_2/\text{HfO}_2$  ratio is decreased to 10 - 12 (Table 1, analyses 8-13).

#### Cyrtolites from Beryl-Muscovite Pegmatites

Very rarely cyrtolite is found in the blocky zones of beryl-muscovite pegmatites. In this case it occurs in euhedral crystals entirely enclosed in large pods of triphyllite or, less commonly, of quartz. We have seen early beryl and tourmaline crystals bordered with well-formed crystals of black cyrtolite. Analyses of such cyrtolites from Turkestan showed that they have the same  $\text{ZrO}_2/\text{HfO}_2$  ratio as the cyrtolites of the preceding type (Table 1, analysis 14).

#### Cyrtolites Characteristic of the Strongly Albited Pegmatites

Small amounts of cyrtolite were found in almost all strongly albited and greisenized pegmatites (sodium subtype of type V in Fersman's classification) usually in very close association with tabular or platy columbite and also with beryl. The quartz which surrounds segregations of columbite and beryl enriched in cyrtolite usually has a dark smoky color. The cyrtolite crystals are sometimes 1 - 2 cm, but more commonly, 0.5 to 0.8 mm in length; they are light-brown, dipyrimal, and have deformed convex faces with tile-like surfaces. Sometimes the crystals are flattened and platy. Cyrtolite of this type usually forms characteristic rims about the plates of columbite; less commonly it is penetrated by columbite and sometimes occurs as inclusions in the columbite-tantalite crystals.

The occurrence of this type of cyrtolite in the albited areas in close association with albite and columbite or columbite-tantalite suggests that it is formed at the beginning of the albition of pegmatites.

Cyrtolites from the albited zones have high  $\text{HfO}_2$  content (5-7%) and their  $\text{ZrO}_2/\text{HfO}_2$  ratio ranges from 8 to 12.

#### Late Cyrtolite in Replacement Pegmatites with Rare Metals

This group includes various late cyrtolites obviously formed after albition. The character of occurrence of these minerals, their crystal habit, and color are different in different localities. Sometimes they occur in small, almost flat greenish crystals (naegite) in the cracks in albite. Sometimes, as minute dark reddish-brown segregations among the aggregates of fine-grained lepidolite. Occasionally, late cyrtolites are found also among the sulfides (arsenopyrite, bismuthinite) as radiated acicular orange-red crystals, in the cavities in albite. The characteristic feature of the late cyrtolites is the complexity of their composition. Spectrographic analysis shows that they are enriched in calcium, beryllium, phosphorus, niobium, and sometimes in arsenic and barium. The late cyrtolites of complex composition are sometimes described in the literature as alvite (beryllium and aluminum-bearing cyrtolite), oyamalite (phosphorus-bearing

Table 2

Variation in  $\text{HfO}_2$  Content in Different Generations of Zircon from Granite Pegmatites

Type of pegmatite	Variety of zircon	Crystal form	Color	Paragenesis	$\text{HfO}_2$	$\text{ZrO}_2/\text{HfO}_2$
Plagioclase-microcline-biotite	Zircon	Small elongated prisms	Rose	Biotite, garnet	0, 7-1.4	46-89
Plagioclase-microcline-uranium-rare earths	Cyrtolite	Short columnar, flattened and dipyrimal	Red-brown	Apatite, ilmenite		
	Cyrtolite		Light-brown	Xenotime, monazite, allanite, uraninite, garnet, muscovite fergusonite	2, 7-6.1	9-21
Microcline-beryl-muscovite	Cyrtolite	Short columnar	Reddish-brown, black	Beryl, tourmaline, triphyllite, apatite	3.3	17.3
Albite-microcline-beryl with tanta-late	Cyrtolite	Dipyramidal crystals with deformed faces	Light-brown	Columbite, beryl	5, 3-7.4	8-11.5
Albite-microcline, albite-spodumene-microcline and albite-lepidolite-microcline	Cyrtolite, alvite, naegite	Flat acicular crystals in radiated aggregates	Grayish-brown	Albite, lepidolite, columbite	6, 6-13.8	3, 7-9.1

cyrtolite), etc. According to the investigations of Hevesy and Tal-Jantzen [9], alvites have a very high hafnium content. Our analyses (Table 1, analyses 19-24) show that the  $\text{HfO}_2$  content in the late cyrtolites varies from 4-6% to 14% (up to 16% according to Hevesy and Tal-Jantzen) and that their  $\text{ZrO}_2/\text{HfO}_2$  ratio ranges from 3 to 10 and is 5 to 7 on the average. The late pegmatitic cyrtolites are the richest in hafnium and may be considered as hafnium minerals.

Table 2 presents all available data on the variation of the  $\text{ZrO}_2/\text{HfO}_2$  ratio in different generations of cyrtolite formed at the different stages of the pegmatitic process.

### Summary

1. As the pegmatitic process develops the  $\text{ZrO}_2/\text{HfO}_2$  ratio changes regularly. The later the minerals of the zircon group in pegmatites, the greater is their concentration of  $\text{HfO}_2$  and the lower the  $\text{ZrO}_2/\text{HfO}_2$  ratio.

2. The early pegmatitic zircons forming before the beginning of the replacement processes do not differ in their  $\text{HfO}_2$  content and  $\text{ZrO}_2/\text{HfO}_2$  ratio from granitic zircons.

3. In the pegmatites genetically related to alkalic syenites or quartz syenites, the  $\text{ZrO}_2/\text{HfO}_2$  ratio in the zircons rises sharply. Thus, from the  $\text{ZrO}_2/\text{HfO}_2$  ratio it is possible to judge, to a certain extent, of the genetic connection between a pegmatite and an intrusive.

4. The metasomatic zircons found in granite pegmatites are quite different in their  $\text{ZrO}_2/\text{HfO}_2$  ratio from the pneumatolytic-hydrothermal zircons of ore veins. In the former the  $\text{ZrO}_2/\text{HfO}_2$  ratio ranges from 3 to 20, while in the latter, as shown in previous papers, it ranges from 25 to 45 and averages 30. Therefore, the  $\text{Zr}/\text{Hf}$  ratio makes it possible to distinguish between the zircons of albitized pegmatites and the zircons of albitites.

5. The latest zircons crystallizing in the last stages of emplacement of pegmatites have the highest  $\text{HfO}_2$  content, reaching 14%, and may be regarded as independent hafnium minerals.

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Received for publication  
November 13, 1958.

# GEOCHEMISTRY OF Nb AND Ta IN THE NEPHELINE SYENITE MASSIFS OF THE VISHNEVYIE MOUNTAINS

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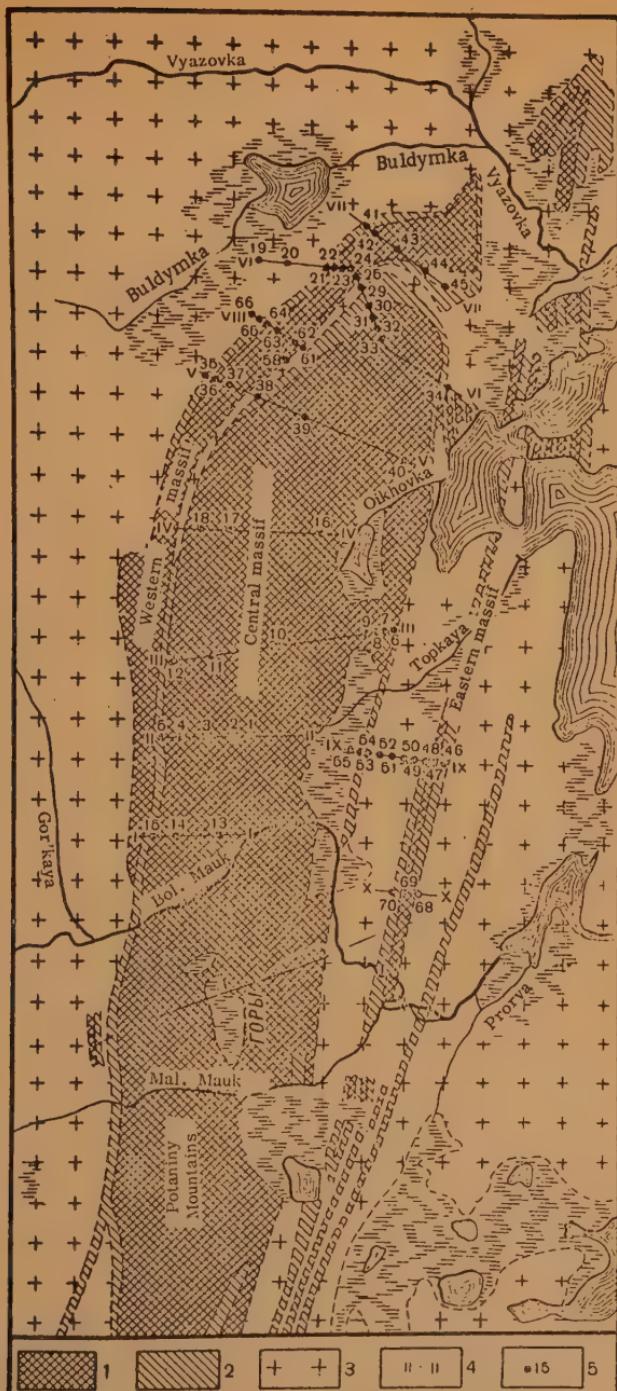
Niobium and tantalum are characteristic rare elements of nepheline syenites, as indicated by their high content in these rocks [1, 2] and the almost invariable presence in nepheline syenites of niobium minerals and ores. The most widespread of the niobium minerals are loparite (in the orthomagmatic rocks) and the minerals of the pyrochlore group (in alkalic pegmatites, albitites, metasomatites, and calcite veins).

The geochemistry of niobium and tantalum in individual nepheline syenite massifs has been discussed by L. S. Borodin [3, 4] and by V. L. Gerasimovskii, M. M. Kakhana, and L. M. Rodionova [5]. But in general, the geochemistry of these elements has not yet received enough attention. The present paper deals with the distribution of niobium and tantalum in the alkalic rocks and minerals of nepheline syenite massifs of the Vishnevye Mountains.

The Vishnevye Mountains contain three nepheline syenite and alkalic syenite massifs: Central, Western, and Eastern (see map). The Central massif, with an area of  $100 \text{ km}^2$ , forms the core of the main anticline. The alkalic rocks of this massif show definite zoning: the central and greater part of the massif is composed of miaskites; these are followed by biotite syenites, and the latter by aegirine-augite syenites. The biotite and aegirine-augite syenites are best developed in the areas separating the Central massif from the Western and Eastern massifs, and form an interrupted band around the miaskites which, locally, are hundreds of meters in thickness. Among the aegirine-augite and biotite syenites, there are lenses of the intruded rocks, granite gneisses, hornblende-biotite gneisses, and, less commonly, amphibolites.

The Western massif, with an area of about  $20 \text{ km}^2$ , is injected into the beds of the western limb of the main anticline. It parallels the Central massif through its entire length. Its structure is similar to that of the Central massif, but its central part consists of alternating miaskites, biotite, biotite-muscovite and, less commonly, aegirine-augite syenites.

The Eastern massif, about  $10 \text{ km}^2$  in area, is composed mainly of



## Geologic map of nepheline syenite massifs of Vishnevye and Potaniny mountains

1 - miaskites, 2 - alkalic syenites, 3 - intruded rocks,  
4 - numbers of sections, 5 - numbers of samples

Table 1

## Niobium and Tantalum Content in the Rocks of The Vishnevye Mountains\*

Rocks and number of samples	Range of content, %			Average content, %			Nb/Ta ratio	
	Nb <sub>2</sub> O <sub>5</sub>	Ta <sub>2</sub> O <sub>5</sub>	Nb <sub>2</sub> O <sub>5</sub>	Ta <sub>2</sub> O <sub>5</sub>	Nb	Ta	Aver- age	Range of variation
Miaskites (87, 5% of the area)	0, 008—0, 080	0, 001—0, 034	0, 036	0, 0026	0, 025	0, 021	11, 8	6, 9—24, 3
Biotite syenites (1, 2% of the area)	0, 002—0, 017	0, 001—0, 006	0, 026	0, 0020	0, 017	0, 016	10, 6	8, 8—13, 5
Aegirine-augite syenites	0, 005—0, 038	0, 001—0, 003	0, 019	0, 0015	0, 013	0, 012	10, 8	7, 8—11, 7
Granite gneisses Il'men' type	0, 002—0, 022	< 0, 001	0, 006	< 0, 001	0, 004	—	—	—
Amphibolites	< 0, 001	< 0, 001	< 0, 001	< 0, 001	—	—	—	—
Serpentinites	< 0, 001	< 0, 001	< 0, 001	< 0, 001	—	—	—	—

\* All chemical determinations of niobium and tantalum in individual and average samples, and in minerals cited in this paper were made by I. I. Nazarenko, A. A. Manukhova and Z. N. Burova in the chemical laboratory of the Institute of Mineralogy, Geochemistry and Crystal Chemistry of Rare Elements, Academy of Sciences USSR.

Note: Comma represents decimal point.

girine-augite syenites with thin layers of biotite syenites and miaskites. Niobium and tantalum are irregularly distributed in the Vishnevye Mountains (Table 1). They are especially characteristic of the alkalic rocks of the region. The highest average content of niobium and tantalum is found in the miaskites. Their content diminishes from miaskites to the biotite and aegirine-augite syenites. The Nb/Ta ratio in the alkalic rocks varies within narrow limits.

In the granite gneisses the average niobium content is considerably lower than in the alkalic rocks and is approximately equal to the Clarke of the element in granites. In the amphibolites and serpentinites the niobium and tantalum content is less than 0.001%.

Thus, there is in the rocks of the Vishnevye Mountains a regular diminution of niobium and tantalum content from miaskites through the alkalic syenites to the intruded granite gneisses, amphibolites, and serpentinites. The average niobium and tantalum content in the nepheline syenites is approximately ten times as great as their average content in granite gneisses. The alkalic syenites (biotite and aegirine), formed as the result of reaction between the nepheline syenite magma and the intruded granite gneisses, occupy an intermediate position, so far as the niobium and tantalum content is concerned, between these two extremes. Usually in the Central and Western alkalic massifs, the biotite and aegirine-augite syenites accompanying miaskites are also enriched in these elements. In the biotite and aegirine-augite syenites of the Central and Western massifs the  $\text{Nb}_2\text{O}_5$  content reaches 0.045% and the  $\text{Tb}_2\text{O}_5$  content, 0.006%, whereas in the same rocks of the Eastern massif the content of these elements does not exceed 0.021% for  $\text{Nb}_2\text{O}_5$  and 0.002% for  $\text{Ta}_2\text{O}_5$ .

Let us consider some of the peculiarities of distribution of niobium and tantalum in miaskites of the Vishnevye Mountains. The highest average niobium and tantalum content characterizes the larger miaskite intrusives. The miaskites of the largest massif in the Vishnevye Mountains are richer in these elements than the miaskites of the Western and Eastern massifs (Table 2). The Nb/Ta ratio in all miaskite massifs is practically the same. The highest concentrations of niobium and tantalum in the miaskites occur near their contacts with intensively albited zones and especially near vertically dipping contacts. Near the western contact zone the average  $\text{Nb}_2\text{O}_5$  content is 0.041%; near the eastern contact zone, it is 0.032%; and in the central zone of the Central massif, 0.0.23%.\*

The rather uniform distribution of these elements in miaskites along the strike of the individual massifs is also characteristic. For the Central massif the average  $\text{Nb}_2\text{O}_5$  content in the northern part is 0.027%, in the middle part, 0.034% and in the southern part, 0.033%.

The average niobium and tantalum content in the nepheline syenite massifs of the Vishnevye Mountains is 0.024% and 0.0020%, respectively, (with the Nb/Ta ratio being 12). This is approximately 10 times as high as the

In computing the average  $\text{Nb}_2\text{O}_5$  content in the different zones of the Central massif, the author excluded the data from the immediate western contact between miaskites and aegirine-augite syenites, which is intensively albited and carbonatized as a result of the later metasomatic processes. The average  $\text{Nb}_2\text{O}_5$  content in this zone is much higher than in normal miaskites, because the replacing solutions circulating in it were strongly enriched in niobium.

Niobium and Tantalum Content in the Miaskites of the Vishnevye Mountains

Table 2

Massifs	Range of content, %		Average content, %			Nb/Ta ratio	Num- ber of sam- ples
	Nb <sub>2</sub> O <sub>5</sub>	Ta <sub>2</sub> O <sub>5</sub>	Nb <sub>2</sub> O <sub>5</sub>	Ta <sub>2</sub> O <sub>5</sub>	Nb	Ta	
Central	0,008—0,080	0,001—0,004	0,038	0,0026	0,025	0,0022	11,8
Western	0,010—0,045	0,001—0,0055	0,026	0,0021	0,019	0,0017	11,2
Eastern	0,012—0,020	0,001—0,002	0,016	0,0013	0,011	0,0010	11,1
							3

Note: Comma represents decimal point.

larkes of these elements in the igneous rocks [2].\* The average niobium content in the nepheline syenites of the Vishnevyye Mountains is near its larke in nepheline syenites in general (0.02% according to V. M. Goldchmidt and 0.031% according to Rankama), while the average tantalum content is 25 times as high as its clarke (0.00008% Ta according to Rankama).

Comparison of the Nb/Ta ratios in some of the nepheline syenite massifs (Lovozero -- 12.8, Vishnevogorsk -- 12, Il'menogorsk -- 11.5, etc.) shows that they vary within a small range between 11.5 and 12.8 instead of eing 387.5 as stated by Rankama [2]. These data cast doubt on the average tantalum content in nepheline syenites computed by Rankama, as has been justly pointed out by V. I. Gerasimovskii [5], especially as Rankama used analyses of only two mixed samples of nepheline syenites in his computation, which is quite insufficient for rocks of such varied composition.

Niobium and tantalum in the alkalic rocks of the Vishnevyye Mountains are concentrated in biotite and in a number of accessory minerals--menite, sphene, zircon, and pyrochlore--and a characteristic association of these minerals is found in each rock type (Table 3).

The miaskites carry mainly pyrochlore, ilmenite, and biotite; sphene is present in small amounts. The average content of these minerals in the miaskites of different massifs varies within the following limits: pyrochlore, 0.03 -- 0.09%; zircon, 0.06 -- 0.29%; ilmenite, 0.17 -- 0.86%; biotite, 3.89 -- 6.24%; and sphene, 0.02 -- 0.29%. Pyrochlore and zircon of the Vishnevyye Mountains are genetically related to albitization and are usually found in the intensively albitized zones of miaskites.

In the alkalic rocks of the Vishnevyye Mountains, two types of albitization can be distinguished. Albitization of the first type in miaskites and biotite syenites is regional. Albite is distributed more or less uniformly in the alkalic rocks over the entire area of the alkalic province of the Urals.

The average content of albitite in these rocks ranges from 15 to 25%. The albite was formed from the postmagmatic solutions separated during the process of crystallization of the alkalic rocks themselves (autometasomatism).

Albitization of the second type is much later than the first. It is localized in the tectonically weakened zones (fractures, faults, contact zones, etc.) and is developed both in the alkalic rocks and in their pegmatites. This type of albitization, unlike the first, extends beyond the limits of the miaskite massifs and alkalic pegmatites. Albitites are the products of this type of albitization.

Ilmenite, biotite, and sphene are not related to albitization. Usually the smaller nepheline syenite intrusives and the contact zones of the miaskite

\* To calculate the average niobium and tantalum content and to determine their distribution in the nepheline syenite massifs of the Vishnevyye Mountains, 70 samples of different rocks taken from 10 geological sections (see map) were selected and analyzed. The average content of these elements was computed with consideration of the areas of distribution of miaskites and biotite syenites but without using the data on their content in the aegirine-albite syenites. The latter were regarded as hybrid rocks (fenites) formed at the exocontact of the nepheline syenite intrusives as a result of metasomatic reworking of the intruded granite gneisses. The biotite syenites are the endocontact rocks of the miaskite intrusives.

Table 3  
 $\text{Nb}_2\text{O}_5$  and  $\text{Ta}_2\text{O}_5$  Content in the Minerals of Alkalic Rocks  
 of the Vishnevye Mountains\*, %

Rocks	Ilmenite		Biotite**		Sphene		Zircon
	$\text{Nb}_2\text{O}_5$	$\text{Ta}_2\text{O}_5$	$\text{Nb}_2\text{O}_5$	$\text{Nb}_2\text{O}_5$	$\text{Ta}_2\text{O}_5$	$\text{Nb}_2\text{O}_5$	
Miaskites (average)	1,95	0,05	0,032	—	—	—	0,02
Central massif	2,21	0,06	—	—	—	—	—
Western massif	0,46	0,04	—	0,80	—	—	—
Biotite syenites	0,99	0,05	0,024	—	—	—	0,05
Aegirine-augite syenites	0,80	0,05	—	0,44	0,08	—	—

\* Niobium-bearing minerals were separated from the average samples of rocks.

\*\* The  $\text{Ta}_2\text{O}_5$  content in biotite and zircon is less than the sensitivity of the chemical methods of analysis (<0.001%).

Note: Comma represents decimal point.

Distribution of  $\text{Nb}_2\text{O}_5$  and  $\text{Ta}_2\text{O}_5$  in Miaskites of the Vishnevye Mountains

Minerals	Average content of the mineral in the rock, %	$\text{Nb}_2\text{O}_5$ and $\text{Ta}_2\text{O}_5$ content, %		Amount of $\text{Nb}_2\text{O}_5$ in a given mineral, %**
		$\text{Nb}_2\text{O}_5$	$\text{Ta}_2\text{O}_5$	
Biotite	4,41	0,032	<0,001	<0,001
Ilmenite	0,73	1,95	0,05	0,01424
Sphene	0,06	0,80	0,11	0,00048
Zircon	0,10	0,02	<0,001	0,00002
Pyrochlore	0,04	62,83*	1,17*	0,02513
Average content in the rock:				
a) mineralogical computation		—	—	0,041
b) chemical analyses		—	—	0,036
				0,0009
				0,0026

\* Average of 21 analyses of pyrochlore from pegmatites.

\*\* Percentage of the total content in the rock.

Note: Comma represents decimal point.

massifs are enriched in pyrochlore. The content of pyrochlore in these areas is 3 to 5 times as high as the average content in miaskites in general. Ilmenite is more widely distributed in the nepheline syenite of the Central massif, and sphene, in the Western and Eastern massifs. Biotite is especially characteristic of the miaskites of the Western and Eastern massifs.

In the biotite syenites containing the same niobium and niobium-bearing minerals as the miaskites, the content of ilmenite is lower (0.34%), the content of biotite and sphene is higher (to 0.21% of sphene), while the content of pyrochlore is about the same. The richer the miaskites in niobium and niobium-bearing minerals, the higher the content of these minerals in the surrounding biotite syenites.

In the aegirine-augite syenites, pyrochlore occurs only in the strongly albitized varieties at the contacts with the miaskites. The niobium-bearing minerals in these rocks are sphene (1.54%) and ilmenite (0.21%).

Table 3 shows that the maximum content of  $\text{Nb}_2\text{O}_5$  and  $\text{Ta}_2\text{O}_5$  is found in the niobium-bearing minerals of miaskites, which are characterized by the highest average content of niobium and tantalum. The content of niobium and tantalum decreases gradually in these minerals from miaskites to the biotite and aegirine-augite syenites.

An idea of the distribution of niobium and tantalum in the alkalic rocks may be gained from an examination of the balance of these elements in miaskites (Table 4) and aegirine-augite syenites (Table 5).

Table 4 shows that in the miaskites of the Vishnevye Mountains about 40% of all niobium and tantalum is concentrated in titanium-bearing minerals (ilmenite and biotite) and in zircon, the remaining 60% being concentrated in the niobium mineral--pyrochlore.

The agreement between the niobium and tantalum content in miaskites

Table 5

Distribution of  $\text{Nb}_2\text{O}_5$  and  $\text{Ta}_2\text{O}_5$  in aegirine-augite syenites of the Vishnevye Mountains

Minerals	Average content of the mineral in the rock, %	$\text{Nb}_2\text{O}_5$ and $\text{Ta}_2\text{O}_5$ content, %			
		in the mineral		contribution of each mineral to the rock	
		$\text{Nb}_2\text{O}_5$	$\text{Ta}_2\text{O}_5$	$\text{Nb}_2\text{O}_5$	$\text{Ta}_2\text{O}_5$
Sphene	1.54	0.44	0.08	0.0085	0.0012
Ilmenite	0.21	0.80	0.05	0.0017	0.0001
Average content in the rock:					
a) mineralogical computation	-	-	-	0.0085	0.0013
b) chemical analyses	-	-	-	0.019	0.0015

obtained by mineralogical calculation and by chemical analyses of average samples indicates that niobium is concentrated mainly in pyrochlore and in titanium minerals in which, because of the similarity of its crystallochemical properties to those of titanium, it replaces the latter diadochically. No dispersion of niobium in the minerals of other elements is observed. This is confirmed by the fact that the determinations of niobium and tantalum in nepheline, microcline, calcite, and albite showed that its content in these minerals is below 0.001%.

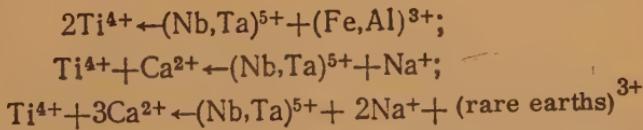
The discrepancy in the figures for the average tantalum content obtained by different methods (Table 4) may be ascribed to the low sensitivity of the chemical method for the determination of tantalum. This made it impossible to determine tantalum in zircon and the widespread biotite.

In the aegirine-augite syenites, as has already been mentioned, niobium and tantalum are concentrated mainly in sphene and ilmenite (Table 5).

The  $\text{Nb}_2\text{O}_5$  and  $\text{Ta}_2\text{O}_5$  content in aegirine-augite was not determined, but the great difference between the average niobium content obtained by chemical analyses and by mineralogical calculations suggests that it may be present in aegirine-augite.

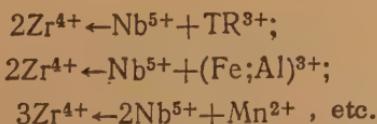
An examination of the distribution of niobium and tantalum in the minerals of the alkalic rocks of the Vishnevyye Mountains shows that during the crystallization of the rocks these elements are fixed as diadochic substitutes, mainly in the titanium minerals and to a less extent in zircon, and also form an independent niobium mineral--pyrochlore. The diadochic substitution of niobium and tantalum for titanium and zirconium is always accompanied by the simultaneous entry into the lattice of cations or anions with lower charges.

In the diadochic substitution of niobium and tantalum for titanium in ilmenite the following schemes are the most probable:



The last two schemes are characteristic of sphene only. It is probable also that in sphene titanium may be replaced by niobium and tantalum with simultaneous replacement of a part of oxygen by fluorine.

The constant presence of small amounts of niobium pentoxide (0.02--0.05%  $\text{Nb}_2\text{O}_5$ ) in zircon of the miaskites and biotite syenites and the absence of inclusions of niobium minerals in zircon suggest that zirconium may be diadochically replaced by niobium in the crystal lattice of zircon. In the substitution of the tetravalent zirconium by pentavalent niobium, the charges are evidently compensated by the entry into the zircon lattice of the rare earths, ferric iron, and other elements. The substitutions in this case probably take place as follows:



The biotite of the alkalic rocks of the Vishnevyye Mountains, unlike the

biotite of some granitic massifs [6], is not the main carrier of niobium in these rocks. In the miaskites and biotite syenites, only 3-5% of the total amount of niobium is fixed in biotite. Apparently, niobium replaces titanium in this mineral. The  $TiO_2$  content in the biotite from the Vishnevye Mountains miaskites reaches 5%.

During the initial stage of crystallization of miaskites and biotite syenites of the Vishnevye Mountains, the concentration of niobium and tantalum was low (hundredths of one percent). Inasmuch as niobium and tantalum did not enter into the crystal lattices of microcline and nepheline, which constitute 80-90% of the alkalic rocks by volume, the absolute concentration of niobium and tantalum increased sharply towards the end of crystallization. The later history of niobium and tantalum was determined by the higher titanium content in the nepheline syenite during the emplacement of magma as compared with the niobium content. The average titanium content in the nepheline syenites of the Vishnevye Mountains is 15 to 20 times as high as that of niobium.

The main mass of titanium minerals--ilmenite and biotite--was formed during the early stages of crystallization of nepheline syenites. The similarity in the crystal chemical properties of titanium and niobium led to the dispersion of a considerable amount of niobium and tantalum ( $\sim 40-50\%$ ) in the titanium minerals. Moreover, other conditions being equal, the more biotite and ilmenite was formed in an alkalic rock and the smaller amount of the independent mineral, pyrochlore, was formed in it during the later stages of crystallization.

In the nepheline syenites of the Vishnevye Mountains, in contradistinction to other nepheline syenite massifs (Khibina, Lovozero and others), in which zirconium predominates strongly over niobium (0.16%  $ZrO_2$ , 0.015%  $Nb_2O_5$  in the Khibina massif; 0.74%  $ZrO_2$  and 0.12%  $Nb_2O_5$  in the Lovozero massif), the average content of these elements is more nearly equal (0.06%  $ZrO_2$  and 0.036%  $Nb_2O_5$ ). For this reason there was no separation in time between the formation of zirconium and niobium minerals in the miaskites and biotite syenites of the Vishnevye Mountains. Zircon and pyrochlore crystallized in these rocks from the rest magma at the latest stages of solidification. Therefore, zirconium did not substantially affect the migration of niobium during the course of crystallization of these rocks.

It is unlikely that the absolute tantalum increased during the period of crystallization of the dark minerals of alkalic rocks (biotite and ilmenite) which contain the main mass of titanium (90-95%). Although biotite and ilmenite constitute only 4-5% of the alkalic rocks by volume, a considerable part of niobium and tantalum is fixed in them in the form of diadothic substitutes. Further behavior of these elements depended largely on the concentration of niobium relative to titanium. An idea of the concentration of niobium at the different stages of crystallization of alkalic rocks may be obtained from the  $Nb/Ti$  ratios in the minerals of these elements. At the earliest stage of crystallization of nepheline syenites, the absolute concentrations of titanium and niobium increased proportionately, for these elements did not enter into nepheline and microcline, and niobium did not become relatively more concentrated than titanium. For this reason, during the formation of ilmenite in the next stage of crystallization, the niobium-titanium ratio was about the same as in the magma ( $Ti/Nb = 14-18$ ). After the crystallization of ilmenite and biotite, when almost all titanium was fixed in the solid phase, the concentration of niobium with respect to titanium in the rest magma increased and conditions became favorable for the formation of the independent niobium mineral, pyrochlore. A number of

ctors favored the crystallization of pyrochlore from the alkalic magma of the Vishnevye Mountains in spite of its relative poverty in niobium and tantalum.

1. The alkalic magma of the Vishnevye Mountains had a low titanium content (0.29%), only half of the average titanium content in nepheline syenites (0.52% according to Daly [7]). This caused a relatively higher concentration of niobium with respect to titanium both at the early and the late stages of crystallization of the alkalic magma than is found in nepheline syenites in general and in some nepheline syenite massifs in particular.

2. Niobium and titanium differed in their geochemical behavior during the crystallization of the alkalic rocks of the Vishnevye Mountains. The main mass of titanium went into the formation of independent titanium minerals at the early stages of crystallization, while a considerable part of the niobium, tantalum, and zirconium remained in the melt.

3. There was only a limited diadochy between titanium and niobium in the titanium and titanium-bearing minerals of the early stages of crystallization of the nepheline syenites.

Tantalum accompanied niobium during all stages of crystallization of the alkalic rocks of the Vishnevye Mountains, and because of the close similarity of its crystallochemical properties to those of niobium and its much lower average concentration, it did not form independent minerals but became concentrated in the niobium and niobium-bearing minerals.

A number of general conclusions concerning the geochemistry of niobium and tantalum in the nepheline syenites of the Vishnevye Mountains can be drawn from the material presented above.

1. The nepheline syenites of the Vishnevye Mountains are characterized by a relatively high niobium and tantalum content which is approximately ten times as high as their content by weight in the igneous rocks in general.

The Nb/Ta ratio in the alkalic rocks of the Vishnevye Mountains varies from 10.6 to 11.8.

2. The miaskites have the maximum average niobium and tantalum content among the rocks of the Vishnevye Mountains. The average content of these elements decreases regularly from miaskites to the biotite and aegirine-augite syenites. The average niobium and tantalum content in the granite gneisses is one-tenth of that in the alkalic intrusives.

3. A relatively high content of niobium and tantalum in the nepheline syenite massifs of the Vishnevye Mountains is localized in the strongly albitized contact zones between miaskites and aegirine-augite syenites.

4. A considerable part of niobium and tantalum (40-50%) in the nepheline and alkalic syenites is concentrated in titanium and titanium-bearing minerals (ilmenite, sphene, and biotite), in which niobium and tantalum substitute diadochically for titanium. Niobium and tantalum are absent from minerals which do not contain titanium.

The  $\text{Nb}_2\text{O}_5$  and  $\text{Ta}_2\text{O}_5$  content in the niobium-bearing minerals decreases gradually from miaskites to the biotite and aegirine-augite syenites.

5. The formation of the independent niobium mineral, pyrochlore, in the latest stages of crystallization of miaskites and biotite syenites was favored by the relatively low concentration of titanium in the alkalic magma and by the limited diadochy between niobium and tantalum and titanium in the early stages of crystallization.

6. The main difference in the geochemical behavior of niobium and tantalum and titanium is in the fact that titanium entered into the rock-forming minerals and formed its own minerals at the earlier stages of the crystallization of nepheline syenites, while a considerable part of niobium

and tantalum remained in the melt.

7. During the crystallization of the nepheline syenites of the Vishnevye Mountains, there occurred both absolute and relative concentration of niobium and tantalum as compared with titanium. In the alkalic rocks of the Vishnevye Mountains, in contradistinction to the agpaitic nepheline syenites, zirconium did not noticeably influence the geochemical behavior of niobium and tantalum.

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Received for publication  
October 3, 1958.

# DISTRIBUTION OF RARE EARTHS IN THE PEGMATITE MINERALS OF NORTHWESTERN AND SOUTHWESTERN KARELIA

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In northwestern and southwestern Karelia there are numerous well differentiated quartz-plagioclase-microcline pegmatites containing a large number of rare earth minerals. Besides the zones of primary quartz-plagioclase-microcline crystallization which play the principal role in the structure of the pegmatites, there are metasomatic zones bordering the pegmatite cores. The following zones can be distinguished in the direction from the borders towards the cores of the dikes:

1. The quartz-albite-oligoclase zone with apographic texture, 1 to 5 m width.
2. The zone of coarse-grained albite, 1-5 m wide.
3. The zone of muscovite in large sheets, 0.5 to 2 m wide.
4. The pods and fracture fillings of saccharoidal albite and greisen muscovite in sheets up to 2 m across.

The accessory rare earth minerals in the pegmatites of northwestern Karelia are sharply divided into two groups, each of which is related to a finite stage of replacement [1]. The first group of rare earth minerals, mainly monazite and allanite, is intimately associated with the coarse-grained albite and muscovite replacing complex. The relicts of microcline allanite found in the zone of coarse-grained albite, and the localization of allanite in some of the pegmatites directly on the peripheries of the microcline perthite blocks in the central zones of the pegmatites (cores) indicate that these minerals were formed during the initial stages of albition as a result of direct replacement of microcline. The second group of minerals represents a later stage in the formation of pegmatites, and is related to the activity of late residual solutions circulating within the regions of development of replacing complexes and also in fractures in the pegmatite cores. The rare earth minerals belonging to this group are monstrandine and two varieties of pyrochlore, obruchevite and rare earth metatite. From 48 to 62% of the rare earths in these minerals are represented by yttrium, gadolinium and dysprosium (see Table). Among the yttrium earths, regarding Gd as belonging to the yttrium earths, Sm is

Composition of the Rare Earths in the Pegmatitic Minerals of Northwestern and Southwestern Karelia

No.	Mineral	Region	La	Ce	Pr	Nd	Sm	Eu	Sum of cerium earths
1	Monazite	N. W. Karelia	18,5	35,6	6,7	22,2	9,55	—	92,55
2	Allanite	"	13	35	8	21	8	0,3	85,30
3	Blomstrandine	"	1,3	5	1,8	6	6,4	0,2	20,7
4	Obruchevite (black)	"	1,3	2,5	0,8	2,5	16	0,2	23,3
5	Obruchevite (brown)	"	2,7	4,5	1,2	5,8	14,6	0,2	29,00
6	Betafite (with rare earths)	"	2,4	8,6	2	10	20	0,4	43,40
7	Monazite	S. W. Karelia	23,4	33,4	8,0	21,7	7,7	—	94,20
8	Allanite	"	21,3	34,2	6,9	18,1	5,4	—	85,90
9	Euxenite (L. Lokka's wilkite)	"	—	2,6	1,1	3,4	4,1	—	11,20
10	Obruchevite (L. Lokka's dark-brown wilkite)	"	—	—	—	—	—	—	—
11	Betafite (L. Lokka's yellow wilkite)	"	—	10,7	3,7	11,5	8,00	—	33,9

Note: Comma represents decimal point.

Table (Cont'd.)

Gd	Tb	Dy	Ho	Er	Tu	Yb	Lu	Y	Sum of yttrium earths	Analy st
5,10	0,45	1,40	0,22	0,22	—	—	—	—	7,09	R. L. Barinskii
5	0,8	7	0,6	0,8	0	0,3	0	14,5	"	"
6,8	1,1	6,5	1,4	3,8	0,9	5	0,9	52,9	79,3	"
24	4	16,2	1,5	4	0,70	3,0	0,9	22,4	76,70	"
25	2,8	12,6	1,3	2,2	0,6	1,3	0,2	25	71,0	"
21	3,20	12,5	1	2	0,5	1,5	0,6	14,6	56,9	Th. Sahama and
5,4	—	1,3	—	0,77	—	—	—	—	7,47	V. Väätäalo [5]
4,8	—	1,0	—	0,6	—	—	—	7	13,4	"
6,0	1,9	8,6	2,4	5,9	1,7	9,4	2,8	50,4	88,8	"
5,80	1,45	7,50	1,15	5,80	1,8	11	3,00	49	86,2	"
7,5	1,40	11,1	1,50	3,78	—	—	4,66	1,16	35	66,10

Note: Comma represents decimal point.

strongly predominant and its content reaches 14 to 20% of the total content of rare earths.

Obruchevite and the rare earth betafite occur in fractures cutting the coarse-grained albite or, less frequently, the blocky quartz.

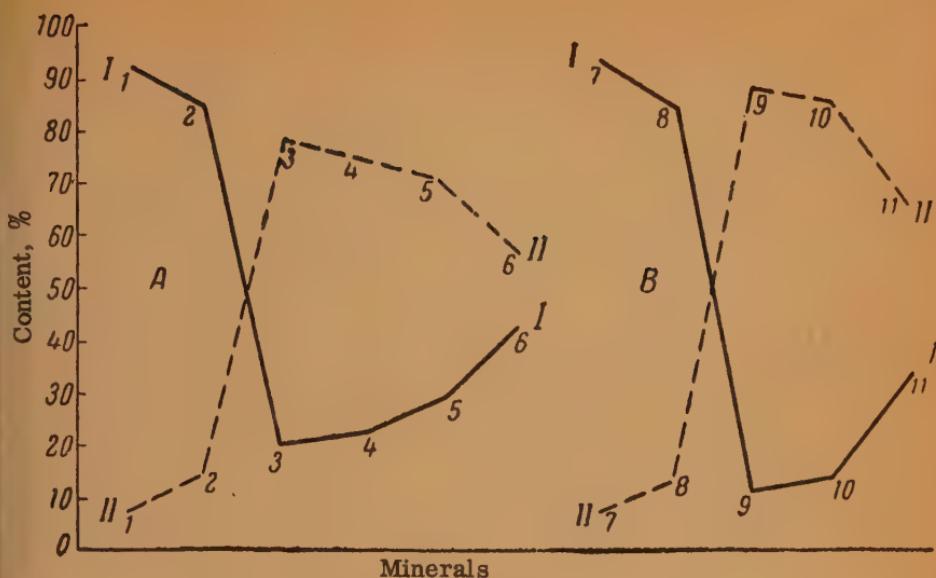
It has been established that blomstrandine formed later than allanite and monazite, but earlier than obruchevite. The accessory rare earth minerals in the pegmatites of southwestern Karelia are allanite, monazite, euxenite, obruchevite and betafite. The main mass of these minerals is localized in the pegmatite cores and is intimately associated with large sheets of biotite developed along fractures. Euxenite, obruchevite and betafite were formerly described under the common name, "wiikite" [2, 3, 4, 5].

The presence in the pegmatites of northwestern and southwestern Karelia of the earlier rare earth minerals (monazite, allanite, euxenite, blomstrandine) together with the later minerals formed by replacement of the earlier ones\* deserves special attention. The development of yellow betafite (Table, No. 11) at the expense of black crystals of euxenite (No. 9) is very clearly seen in the pegmatites of southwestern Karelia. In some cases a multistage replacement of one variety of a mineral by another may be observed. For example, black obruchevite (No. 4) is replaced by brown obruchevite (No. 6). Brown obruchevite is replaced by green rare earth betafite (No. 6), and the latter, in its turn, is often replaced by yellow uranium betafite. A detailed study of the relationships among the minerals established the sequence of their formation during the evolution of the pegmatitic melt-solution. The sequence of formation of all rare earth minerals in the pegmatites of the regions under investigation reveals the geochemical behavior of the rare earths of the cerium and yttrium groups both in the earlier stages of the pegmatitic process and during the later metasomatic processes. Because of the close resemblance between the pegmatites of northwestern and southwestern Karelia, both as to the paragenetic association of the rock-forming and rare earth minerals and as to the internal structure, it may be concluded that the geochemical behavior of the rare earths is the same in the pegmatites of both regions.

When the minerals are arranged in the order of their formation, from earliest to latest, and a graph is drawn (see diagram) on the basis of their content of the rare earths, it is easily seen that the cerium earths separate earlier than the yttrium earths. The earlier minerals, allanite and monazite, contain mainly the cerium earths. After the separation of the cerium earths, the pegmatitic liquid becomes strongly enriched in the heavier lanthanides and yttrium. Then replacement of the earlier minerals by the later ones begins. In the pegmatites of northwestern Karelia, obruchevite forms after columbite and, as has already been mentioned, the earlier varieties of minerals are replaced by the later ones. In the pegmatites of southwestern Karelia, columbite is replaced by obruchevite, and euxenite, by betafite. In the process of replacement of one mineral or variety by another, each later "secondary" mineral acquires a relatively higher content of the lighter lanthanides, especially Ce, Nd and Sm, as compared with the mineral which it replaces.

Betafite (Table, No. 11) has a relatively higher content of the cerium

\* Metasomatic minerals and their varieties will be called "secondary" in what follows.



Variation in the composition of the rare earths in the pegmatite minerals of Karelia

I -- Content of the cerium earths  
 II -- Content of the yttrium earths

A. Northwestern Karelia

- 1. Monazite
- 2. Allanite } earlier minerals
- 3. Blomstrandine }
- 4. Obruchevite, black } later, "secondary" minerals
- 5. Obruchevite, brown }
- 6. Rare earths betafite }

B. Southwestern Karelia

- 7. Monazite
- 8. Allanite } earlier minerals
- 9. Euxenite }
- 10. Obruchevite } later, "secondary" minerals
- 11. Betafite }

earths than the euxenite which it replaced (No. 9). The same regularity is confirmed by the example of black and brown obruchevite and the rare earth betafite. In the latter, the content of the cerium earths is little less than of the yttrium earths. While the independent cerium and yttrium minerals are typically selective, the composition of the rare earths in betafite is mixed.

The earlier appearance of the cerium minerals as compared with the yttrium minerals during the pegmatitic process was observed by Ingerson [6]

in the pegmatites of Minas Gerais (Brazil).

What is the explanation of the relative enrichment of the later metasomatic varieties of the rare earth minerals in the heavier lanthanides?

A certain range of variation in the composition of the rare earths in such varieties of pyrochlore as black and brown obruchevite and the rare earth betafite is possible because of the 8-fold coordination of the rare earths replacing Ca in the mineral lattices. In the minerals with intermediate coordination numbers (7-9) cerium and the yttrium earths may be present at the same time [7]. However, the above example shows that, in spite of the 8-fold coordination of the rare earths, their composition in obruchevite is strictly selective and favors the yttrium group, while in betafite it is mixed (Table). The factual data suggest that the relative enrichment of the "secondary" later varieties of cerium minerals in rare earths is explained by different basicity and, therefore, different mobility of the complex compounds of the cerium and yttrium earths forming during the replacement of one variety by another. In the opinion of A.A. Beus [8], "The change in the pH determining the hydrolysis of the complex compounds of rare earths and their separation in the solid phases under conditions of increasing alkalinity of the solutions is an important and constantly active factor in the concentration of the rare earths." It is possible that the regular change in the pH leads to a fractional separation of the rare earths during the replacement of one mineral by another.

During the process of metasomatism, the yttrium earths are more mobile; they are leached out and serve as the source for the formation of the new still later yttrium minerals.

On the walls of a fracture in the coarse-grained albite from Alakurtti, near an aggregate of black obruchevite partially replaced by brown obruchevite, which in its turn is replaced by the green rare earth betafite, there are small rosettes of a still later pink mineral, which, according to preliminary examination, is an yttrium silicate.

### Summary

1. A geochemical study of the rare earths shows that in the process of pegmatitization the cerium earths are separated at the earlier stages of replacement, while the yttrium earths are concentrated during the later stages of mineral formation.

2. As a result of action of the late solutions on the selective yttrium minerals, "secondary" minerals are formed metasomatically which are characterized by a low content of yttrium earths. This is due, apparently, to the considerably greater mobility of the yttrium earths in solutions with a higher concentration of strong bases.

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Received for publication  
October 17, 1958.

## GEOCHEMISTRY OF GALLIUM IN THE GRANITOIDS OF THE SUSAMYR BATHOLITH (CENTRAL TIEN SHAN)

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Gallium is a typical dispersed element very intimately associated with aluminum during magmatic processes. For this reason, the gallium ion almost exclusively substitutes for aluminum ion in minerals of igneous rocks. This means that in granitoids, gallium is found in practically all rock-forming minerals. It should be mentioned, however, that gallium content in quartz is usually very low, variable and largely accidental.

The intimate geochemical relationship between gallium and aluminum is due to the close similarity of such crystal chemical properties as ionic radii and valences ( $Al^{3+} - 0.57A$ ;  $Ga^{3+} - 0.62A$ ).

But although gallium is very similar to aluminum, it differs from it in a number of properties. In particular, gallium has a considerably higher ionization potential, which makes it akin to the chalcophile elements. This is probably the reason why, in the process of ore formation, gallium accompanies such chalcophile elements as zinc and is enriched in sphalerites.

It may be said that the geochemical nature of gallium is twofold: in magmatic processes it is lithophile and closely associated with aluminum, while in hydrothermal processes it is chalcophile.

Gallium is one of those rare elements for which a considerable body of experimental data presently exists. The data on its occurrence in the igneous rocks it is necessary, first of all, to point out that the bulk of this element in rocks is fixed in rock-forming minerals containing aluminum. A very small portion of gallium is held in accessory minerals, although in some of them (spheene, ilmenite) it may occur in noticeable amounts by ionically substituting for  $Fe^{3+}$  and  $Ti^{4+}$ .

An investigation of the distribution of gallium among the monomineralic fractions of typical granitoids of the Susamyr batholith illustrates all of the peculiarities of its distribution among the minerals of this type of rocks. Results are presented in Table 1.

Table 1 shows that the main mass of gallium in the granitoids is found in

Table 1

Distribution of Gallium Among the Minerals in the Granitoids  
of the Susamyr Batholith

Mineral	Content of mineral in rock (Wgt. %)	Ga content in mineral, (PPM)	Part of the total Ga in the rock contained in the mineral,	Part of the total Ga in the rock contained in the mineral, %	Total Ga content in the rock (PPM)
Melanocratic granodiorite					
(Northern Kavak Range)					
Quartz	18.5	5	0.9	4	
Plagioclase	55.0	25	13.7	65	
Potash feldspar	12.0	12	1.4	7	72
Hornblende	4.0	18	0.7	3	
Biotite	10.0	45	4.7	21	
Total			21.4		16
Inequigranular granite					
(Dzhumgol Range)					
Quartz	35.3	2	0.7	4.5	
Plagioclase	28.2	20	5.6	37.5	
Potash feldspar	31.3	12	3.8	25.5	63.0
Biotite	3.7	70	2.6	17.5	
Total			12.7		15

feldspars (63-72%). Plagioclase-feldspars always contain more gallium than potash feldspars. The highest gallium content is found in biotite, which, in the granitoids, may contain 20% of the gallium in the rocks.

In examining the distribution of gallium among minerals, one of the most important aspects of the crystal chemistry of gallium is its substitution for aluminum in fourfold and sixfold coordination. The somewhat larger ionic radius of gallium (0.62A) suggests that those structures will be more stable in which gallium replaces six-coordinated rather than four-coordinated aluminum.

The question of preferred concentration of gallium in minerals may be satisfactorily answered with the aid of its concentration coefficients in different minerals associated with each other. For this purpose it is convenient to use Nockolds and Mitchell's (1952) data on the granitoids of western Sotland. The gallium concentration coefficients in these rocks are as follows:

Minerals	Number of samples	Concentration coefficients ( $\frac{\text{Ga/Al in minerals}}{\text{Ga/Al in rock}}$ )
Potash feldspars	6	0.85
Plagioclase feldspars	7	1.2
Hornblendes	5	2.0
Biotites	9	2.1

These figures show that in those minerals in which aluminum has both fourfold and sixfold coordination the concentration coefficient of gallium is usually almost twice as high as in the minerals in which aluminum is present in fourfold coordination only.

On the basis of concentration coefficients feldspars obviously cannot be considered as concentrators of gallium, while hornblendes and biotites can. However, since gallium does enter into lattices in which aluminum has four-fold coordination, the bulk of gallium is fixed in feldspars; they must be considered, therefore, as the principal carriers of gallium in the granitoids.

In general, the characteristics of gallium distribution in granitoids of the Susamyr batholith and the data on its occurrence in granitoids of other regions clearly indicate its intimate geochemical and crystal chemical association with aluminum, and this must be reflected in the geochemical history of gallium during magmatic differentiation.

Quite instructive from this point of view are data on the distribution of gallium in a genetically related series of rocks. The granitoids of the Susamyr batholith provide an excellent example. In the principal magmatic complex of this region, belonging to the Caledonian tectonic-magmatic cycle, there are three intrusive phases. The rocks of the first phase--diorites and gabbro-diorites-- have a very limited distribution. The most widespread rocks are granites and granodiorites of the second (main) intrusive phase. The leucocratic granites of the third phase occur in a series of plutons but occupy a considerably smaller area than the granitoids of the main phase. The latest differentiates of the large magma body are aplite dikes and aplitic granites. In addition to the granitoids of the principal Caledonian complex of the Susamyr batholith, the region contains an independent younger intrusive phase of biotite granites of the Boorteke-Kavak type.

The results of our investigation are collected in Table 2, which gives gallium and aluminum ratios in the rocks, in addition to their gallium content.

As can be seen from the data of Table 2, the gallium content in the rocks of the principal Caledonian complex of the Susamyr batholith as a whole is slight. In the rocks of its main intrusive phase, the gallium content ranges from 12 to 25 PPM; i.e., the maximum concentration is double the minimum. But in most (85%) of the samples the amount of gallium is between 15 and 20 PPM. In the leucocratic granites of the next intrusive phase the concentration of gallium varies within very narrow limits, between 15 and 18 PPM. Only in one sample is its content as low as 13 PPM. However, the constancy of gallium content in the leucocratic granites cannot be considered well established, because only a few samples of these granites were analyzed.

Table 2

## Distribution of Gallium in the Granitoids of the Susamyr Batholith

Intrusive phases	Rocks	Sample No.	Locality	Ga content in rocks, (PPM)	Ga · 10,000 / Al
Phase I of the principal complex	Diorite " " "	11/55 98/53 1256 623	N. Kavak Dzhumgol Susamyr Susamyr	20 22 22 14	
				19	
Phase II of the principal complex	Average gallium content in phase I Melanocratic granodiorite " " Porphyritic granodiorite Porphyritic granodiorite Quartz diorite Porphyritic granodiorite Porphyritic granite Porphyritic granodiorite Adamellite Granodiorite Porphyritic granodiorite Non-equigranular granite Melanocratic adamellite Porphyritic granodiorite Porphyritic granodiorite Porphyritic granodiorite Quartz diorite Melanocratic granodiorite Porphyritic granodiorite	284 99/53 1331 1239 7/55 27a/55 455 XII XIII 238 1254 1209 60/54 701 1/53 1201 211 62/54	Dzhumgol " " " " " " N. Kavak Dzhumgol Sarykamysh Susamyr Dzhumgol " " Sarykamysh Dzhumgol Sarykamysh Susamyr N. Kavak " " " " " " Sarykamysh	20 16 16 20 25 14 18 15 15 18 15 12 17 17 13 15 16 19	- - - - - 0.7 0.9 - 0.8 0.8 0.7 0.8 0.6 0.7 0.8 0.8 0.6 0.8 -

Table 2 (Cont'd.)

Distribution of Gallium in the Granitoids of the Susamyr Batholith

Intrusive phases	Rocks	Sample No.	Locality	Ga content in rocks, (PPM)	Ga · 10,000 Al
	Porphyritic granodiorite	462	Sarkamyrsh	18	-
	Porphyritic granodiorite	2b/55	N. Kavak	13	0.7
	Porphyritic granodiorite	276	Dzhumgol	16	0.8
	Porphyritic granite	55a/54	Susamyr	16	0.8
	"	11/54	"	17	0.8
	Porphyritic granodiorite	11/55	Dzhumgol	20	0.9
	Non-equigranular granite	12226	"	20	1.0
	Porphyritic granodiorite	12119	"	20	0.9
	Quartz diorite	12000	N. Kavak	19	-
	Tonalite	274	Dzhumgol	20	0.8
	Porphyritic granodiorite	1207	Sarykamysk	19	0.9
	"	1297	Susamyr	15	0.7
Average gallium content in phase II					
Phase III of the principal complex	Pink leucocratic granite	480	Dzhumgol	17	-
	"	56/53	"	18	-
	Pink leucocratic granite (slightly altered)	221	Susamyr	15	-
	Gray leucocratic granite	5c/54	Dzhumgol	13	-
	Pink leucocratic granite (slightly altered)	XX	Susamyr	17	0.8
	Pink leucocratic granite	VII	Dzhumgol	18	0.9
	Pink leucocratic granite	251	"	16	0.9
				18	1.0

## Distribution of Gallium in the Granitoids of the Susamyr Batholith

The very slight increase in the gallium content in aplitic granites is possibly due to the fact that it accumulates in small amounts in the final magma phases, enriching them in the last stages of crystallization.

No less interesting is the fact that in rocks of the principal complex, as well as in granites of the Boortek-Kavak type, the Ga/Al ratio remains practically constant. In all analyzed samples the  $\text{Ga} \cdot 10,000/\text{Al}$  ratio averages 0.8. In other words, in all analyzed samples there are 8 gallium atoms for every 100,000 aluminum atoms. Moreover, in more than 80% of the analyzed samples this ratio varies only from 0.7 to 0.9.

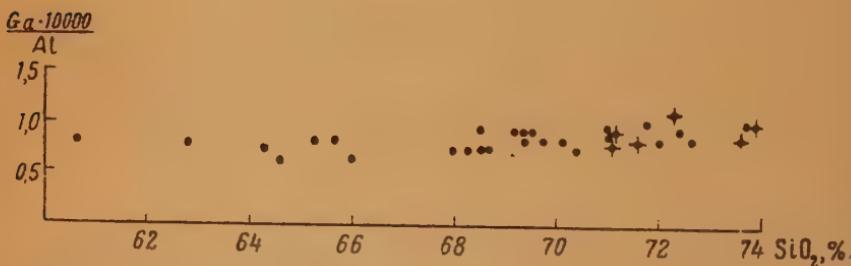
The constancy of the Ga/Al ratio is especially well shown by the diagram, where the  $\text{Ga} \cdot 10,000/\text{Al}$  ratio is plotted on the ordinate and silica content on the abscissa.

The diagram shows that during the process of magmatic differentiation the Ga/Al ratio remains almost constant. This must be considered as the most important geochemical characteristic of the behavior of gallium during the magmatic stage.

At the same time, in the case of the Susamyr batholith the Ga/Al ratio in the granitoids of the principal intrusive complex does not differ from the Ga/Al ratio in the Boortek-Kavak granites belonging to a different complex.

The constancy of the Ga/Al ratio in the rocks of the same magmatic complex may be demonstrated also by the example of the Garabal Hill complex studied by Nockolds and Mitchell (1952).

These authors determined the gallium content in gabbros, diorites, granodiorites and aplites. In all samples the  $\text{Ga} \cdot 10,000/\text{Al}$  ratio was 0.8, except for one sample (coarse-grained gabbro), where it was 1.1.



Gallium aluminum ratios in the granitoids of the Susamyr batholith

- -- granitoids of the principal complex of the Susamyr batholith;
- + -- biotite granites of the Boortek-Kavak type

Thus in this magmatic complex also, the Ga/Al ratio is practically constant. This suggests that, in general, within a single body of granitoid magma the Ga/Al ratio remains practically constant. Inasmuch as during the differentiation of granitoid magmas the aluminum content changes very slightly, the change in gallium content is also slight.

In examining the data on the distribution of gallium in genetically related series of rocks, it is necessary to recall certain conclusions made by V. M. Goldschmidt regarding its geochemistry. In speaking of the distribution of

gallium in rocks of different types, Goldschmidt and Peters (1938) stated, "If igneous rocks are arranged in the order of their position in the course of fractional crystallization, it will be seen that, unlike aluminum, gallium is undoubtedly enriched in the final magmatic phase." This statement was made by Goldschmidt and Peters on the basis of analysis of genetically unrelated and geologically ill defined rock samples from different regions.

The facts presented above show that Goldschmidt's conclusion that gallium is accumulated in the final magmatic phase must be revised.

The example of the granitoids of the Susamyr batholith show that a very small concentration of gallium occurs only in the final stages of differentiation (during the formation of aplite dikes). But in the main differentiation series (main intrusive phases) there is neither an enrichment of gallium in the acid differentiates nor a relative concentration of it with respect to aluminum. This is true also of the granitoid complex of Western Scotland. It may be supposed, therefore, that variations in gallium content are to be ascribed to regional differences in composition of magmatic complexes.

The distribution of gallium in the granitoids of the Susamyr batholith and among their minerals suggests certain conclusions concerning the basic geochemical behavior of gallium in granitoids.

1. Gallium is a typical dispersed element which, during the magmatic stage of its history, has very close geochemical and crystal chemical affinity for aluminum. In granitoid minerals, gallium is found almost exclusively as a diadochic substitute in aluminum-bearing minerals. Because it has a somewhat larger ionic radius than aluminum, it enters preferentially into those minerals in which aluminum has sixfold coordination. If the proportions of different rock-forming minerals in the granitoids are considered, the feldspars, which contain from 60 to 70% of all gallium present in the rock, must be considered as the main carriers of this element. Nevertheless, micas and amphiboles, whose gallium content is always higher than that of the associated feldspars, must be regarded as true concentrators of gallium.

2. The distribution of gallium in the rocks of the main intrusive phase of the Susamyr batholith indicates that gallium content is almost constant in the rocks belonging to the same genetic series. A slight increase in gallium content is observed only in aplite dikes. For the entire exposed area of the Susamyr granitoids under consideration, the average gallium content is 7 PPM.

Within the boundaries of a single magmatic complex the gallium-aluminum ratio remains practically constant, and this must be regarded as a manifestation of the intimate geochemical relationship between these elements during the magmatic stage of their history.

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Received for publication November 13, 1958.

# INVESTIGATION OF GERMANIUM CONTENT IN THE PETROLEUMS OF THE SOVIET UNION

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It is well known that petroleum contains a number of the so-called "trace" elements in notable amounts. Thus, the average content of vanadium in petroleum is  $n \cdot 10^{-3}$ , and of nickel,  $n \cdot 10^{-4}\%$ , while the ash of petroleum from the Paleozoic of the Ural-Povolzh'e region often contains up to 50%  $V_2O_5$ . Thus, petroleum often accumulates certain elements in amounts quite unusual for sedimentary rocks. It is interesting, therefore, to investigate the content of germanium in petroleum.

Germanium was determined by the method developed at the Giretdmet (by V. A. Nazarenko and others [1]). The procedure is as follows: Petroleum, together with the fillers  $CaO$  and  $Mg(NO_3)_2$  is carefully reduced to ash. The ash is dissolved in nitric acid (1:4) and germanium precipitated with ammonium and iron hydroxides, and, after addition of phosphoric acid, distilled in the form of  $GeCl_4$ . The distillate is colored with phenylfluorene dissolved in hydrochloric acid. Quantitative determinations of germanium were made by comparing test solutions with a series of standard solutions.

Colorimetric determinations should be made on solutions whose concentration does not exceed 5%, because in the more concentrated solutions the intensity of coloration is not directly proportional to concentration.

The colorimetric determination of germanium with phenylfluorene is very sensitive, and if the reagents are pure the error varies from  $1-2 \cdot 10^{-6}\%$ . The reduction of petroleum to ash, however, is not a satisfactory procedure, because of the volatility of germanium compounds.

To determine the degree of volatility of germanium, experiments were made in reducing petroleum to ash without addition of  $CaO$  and  $Mg(NO_3)_2$ , i.e., by gradual evaporation of petroleum from a platinum dish, first on a water bath then on a sand bath, until coke formed, which was then completely reduced to ash in a muffle furnace. The results are shown in Table 1.

The data show that the reduction of petroleum to ash without the addition of  $CaO$  and  $Mg(NO_3)_2$  either volatilizes germanium completely or diminishes its content to one tenth or one twentieth. Thus, this is the part of analysis which affects its accuracy and the reproducibility of results. Evidently, very turbulent liberation of gases in reduction of petroleum to ash with an oxidizing agent or ignition of gases causes loss of germanium, and this must be the reason for discrepancies exceeding  $1-2 \cdot 10^{-6}\%$  in some of our analyses.

Results of the investigation of the germanium content of the petroleums of the Soviet Union are given below. Altogether, 81 petroleum samples and

Table 1

Reduction of Petroleum to Ash Without Fillers:  
 $\text{CaO}$  and  $\text{Mg}(\text{NO}_3)_2$

Locality	Germanium content, %	
	in ash obtained with fillers	in ash obtained without fillers
Aznakaev, well 538	$6 \cdot 10^{-6}$	traces
Tarkhany, well 127	$6.9 \cdot 10^{-5}$	$8 \cdot 10^{-6}$
Sultangulovo, well 100	$2.6 \cdot 10^{-5}$	$1 \cdot 10^{-5}$
Artem Island, well 285	$3.2 \cdot 10^{-5}$	traces

2 samples of native bitumen were analyzed.

Oils from Sakhalin Island fields. Petroleum occurs on Sakhalin Island in a series of multi-zone deposits in Tertiary rocks. Analyses were made on thirteen samples taken from the following fields: Katangli, Uiglekuty, Okha, Ekhabi and Eastern Ekhabi. The analyses and the specific gravities of these oils are presented in Table 2.

The content of germanium in the Sakhalin oils is very low and is near the limit of accuracy of determination.

No germanium was detected in a number of samples from Katangli, Ekhabi and Eastern Ekhabi. The oils of Okha have a more constant, although very low, germanium content. The relation between the specific gravity of petroleum and its germanium content is poorly defined. All that can be said is that in the lighter oils (sp. g. 0.82-0.87) germanium is more frequently found in traces or not at all than in the heavier oils with specific gravity of 0.93.

The average germanium content in the Sakhalin oils, all samples considered, is 0.015 g/ton. In the Okha oils, it is 0.02 g/ton.

The oils of Azerbaidzhan. Azerbaidzhan oils, also, occur in Tertiary rocks. Oils from different horizons of the productive beds were analyzed. The samples were taken from the following fields: "Neftyanye Kamni," Artem Island, Binagady, Kala, Lok-Batan, Neftechala, Surakhany, Balakhany and Sabunchi. The analyses are given in Table 3.

Germanium was found in the oils from all fields except Neftechaly (middle Apsheronian, bed II) and Balakhany (Balakhan formation, bed X). In general, germanium content in the oils from all other fields varies within  $1 \cdot 10^{-6}\%$ . Germanium content ten times as high as in the other oils was found in the samples from Artem Island (beds KS<sub>5</sub>a and PK) and Kala (Balakhan formation PK<sub>1</sub>). These oils contain, on the average, 0.2-0.3 g/ton of germanium. The relation between specific gravity and germanium content is not discernible; rather, one may speak of regions enriched in germanium, as in the oils of Artem Island and Kala.

The average germanium content in all investigated samples of

Table 2

## Oils of Sakhalin Island

Age	Bed	Locality	Sp. G.	Ge content	
				%	g/ton
Tertiary	I	Katangli, well 351	0.93	traces	-
	II	" 224	0.93	$2 \cdot 10^{-6}$	0.02
	II	Uiglekuty, well 386	0.93	$2 \cdot 10^{-6}$	0.02
	IV	Okha, well 7288	heavy oil	$2 \cdot 10^{-6}$	0.02
	VII	" 425	heavy oil	$2 \cdot 10^{-6}$	0.02
	XIII	Ekhabi, well 193	0.82	traces	-
	XIV	" 255	0.82	$2 \cdot 10^{-6}$	0.02
	XVI	" 325	0.85	$3 \cdot 10^{-6}$	0.03
	XVII	" 319	0.87	none	-
	XXV	Eastern Ekhabi, well 311		$2 \cdot 10^{-6}$	0.02
	XXII	" " " 252	0.87	none	-
	XXVII	" " " 263	0.87	$2 \cdot 10^{-6}$	0.02
	III	Okha, well 259	heavy oil	$3 \cdot 10^{-6}$	0.03
Average germanium content				$1.5 \cdot 10^{-6}$	0.015

Azerbaidzhan oils is 0.063 g/ton.

The oils of Fergana. In the Fergana valley, oils from Cretaceous and Tertiary beds were analyzed. Samples were taken from the following fields: Maili-Su, Changyr-Tash, Palvantash, KIM, Southern Almyshik and Northern Rishtan. The analyses are given in Table 4.

Small amounts of germanium,  $2-4 \cdot 10^{-6}\%$ , were found in practically all samples. In the oils of Southern Almyshik and Maili-Su, the germanium content is ten times as high as in other oils. They contain up to 0.1 - 0.26 g/ton of germanium. No relation between the specific gravity of oil and its germanium content was observed.

As in the previously reviewed petrolierous regions, high germanium content is found in the oils from some fields whatever the age of the oil producing horizon. Thus, in the Southern Almyshik field, germanium content is high in the oils from the Sumsar and Alai horizons and from Cretaceous beds.

In this field the content of germanium increases with specific gravity:

Southern Almyshik	(Table 4)
Sp. G.	Ge, g/ton
0.88	0.26
0.84	0.20
0.82	0.10

However, there are exceptions: an oil with specific gravity of 0.82 from the Turkestan beds in the same field contains no germanium.

The average germanium content in all oils of Fergana is 0.34 g/ton.

## Azerbaijhan Oils

Age	Formation, horizon	Locality	Sp. G.	Ge content	
				%	g/ton
1	KaC <sub>1</sub>	Neftyanye kamni, well 119	0.901	2 • 10 <sup>-6</sup>	0.02
	KaC <sub>2</sub>	" 273	0.829	2 • 10 <sup>-6</sup>	0.02
2	PK <sub>1</sub>	" 49	0.892	2 • 10 <sup>-6</sup>	0.02
	KC <sub>3</sub>	Artemneft', well 94	0.917	6 • 10 <sup>-6</sup>	0.06
	KC <sub>5 a</sub>	" 295	0.918	1.1 • 10 <sup>-5</sup>	0.11
	PK	" 285	0.916	3.2 • 10 <sup>-5</sup>	0.32
3	KC <sub>1</sub>	Binagady, well 4012	0.8987	traces	-
	KC <sub>6</sub>	" 1168		3 • 10 <sup>-6</sup>	0.03
	PK	" 1171	0.910	4 • 10 <sup>-6</sup>	0.04
4	Balakhany fm., hor. V	Kala, well 148		8 • 10 <sup>-6</sup>	0.08
	Sabunchi fm., bed IV	" 1119		2 • 10 <sup>-6</sup>	0.02
	Surakhany fm., bed CD	" 675	0.877	2.5 • 10 <sup>-6</sup>	0.025
	KC <sub>11-12</sub>	" 1362		none	-
5	Balakhany fm	" 1175		3.2 • 10 <sup>-5</sup>	0.32
	PK <sub>1</sub>	" 1040		2.0 • 10 <sup>-5</sup>	0.20
6	Sabunchi fm., hor. I	Lok-Batan, well 873	0.86	3.4 • 10 <sup>-6</sup>	0.34
	Middle Apsheron, hor. II	Neftechala, well 276	0.895	traces	-
	KC <sub>8</sub>	Surakhany, well 1666	0.862	none	-
	PK <sub>1C</sub>	" 1197	0.888	none	-
7	Surakhani fm., B-C bed	" 714	0.805	2 • 10 <sup>-6</sup>	0.02
	Balakhany fm., bed X	Balakhany, well 318	0.934	none	-
	Middle Apsheron	Sabuchi, well 41221	0.894	8 • 10 <sup>-6</sup>	0.08
				Average germanium content	6.3 • 10 <sup>-6</sup>
					0.063

Table 4  
Oils of Ferghana Valley

Age	Bed	Locality	Sp. G.	Ge content	
				%	g/ton
Sumsar stage	III	Maili-Su, well 28	0.86	$2 \cdot 10^{-6}$	0.02
	III	Changyr-Tash. well 73	0.87	$2 \cdot 10^{-6}$	0.02
	III	Changyr-Tash. well 133	0.88	$2 \cdot 10^{-6}$	0.02
	III	Palvantash, well 205	0.88	$2 \cdot 10^{-6}$	0.02
	III	Yuzhnyi Alamyshik, well 390	0.86	$2.6 \cdot 10^{-5}$	0.26
Rishtan stage	IV	Palvantash, well 224	0.86	none	-
Turkestan stage	V	KIM, well 152	0.85	$2 \cdot 10^{-6}$	0.02
	V	Yuzhnyi Alamyshik, well 3	0.82	none	-
Alai stage	VII	Palvantash, well 36	0.84	$4 \cdot 10^{-6}$	0.04
	VII	Yuzhnyi Alamyshik, well 18	0.82	$1 \cdot 10^{-5}$	0.1
	VII	Maili-Su, well 39	0.88	$1.6 \cdot 10^{-5}$	0.16
	X	Changyr-Tash. well 130	0.84	none	-
	XIII	Palvantash, well 210	0.84	$2 \cdot 10^{-6}$	0.02
Cretaceous	XVI	Severnyi Rishtan, well 5	0.77	$2 \cdot 10^{-6}$	0.02
	XXII	Yuzhnyi Alamyshik, well 200	0.84	$2 \cdot 10^{-5}$	0.2
Average germanium content				$3.4 \cdot 10^{-6}$	0.034

The oils of Bashkiria. Oils from the Devonian beds, from the coal-bearing Lower Carboniferous beds and from the deposits of the Lower Permian Artinskian stage were analyzed. Samples were taken at the following fields: Or'ebash, Shkapovo, Chekmagush, Tuimazy, Vvedenovka, Ishimbai, Kattashevka, Kinzebulatovo, Kazankovka. The analyses are given in Table 5.

All analyzed samples of petroleum contain germanium. The variation in germanium content in the oils from different fields is slight and with one exception does not exceed 0.06 - 0.08 g/ton (a sample of oil from a Carboniferous bed in the Tuimazy field with a germanium content of 0.29 g/ton).

There is a certain relationship between germanium content and age of the oil horizon. The average germanium content in the oils from the Devonian rocks is 0.05 g/ton; in the oils from the Carboniferous beds, 0.027 g/ton; and in the oils from the Artinskian beds, 0.025 g/ton. There is no relation between specific gravity of the oil and its germanium content.

The average germanium content in the Bashkirian oils is 0.044 g/ton.

The oils of Tataria. All oils of Tataria are in Devonian rocks. Oils from 8 localities were analyzed: Minibaev, Sullevo-Tashliyar, Bavla, Abdrahman, Aktash, Aznaekovo, Romashkino and Mordovskii Aktash.

Table 5  
Oils of Bashkiria

Age	Locality	Sp. G.	Ge content	
			%	g/ton
Oil-bearing formation	Or'ebash, well 74	0.89	none	-
	" well 63	0.89	$3.5 \cdot 10^{-6}$	0.035
	Shkapovo, well 42	0.92	$2 \cdot 10^{-6}$	0.02
	Chekmagush, well 37	0.90	$2.5 \cdot 10^{-6}$	0.025
	" well 45	0.90	$2 \cdot 10^{-6}$	0.02
	Tiumazy, well 707		$2.9 \cdot 10^{-5}$	0.29
	" well 36		$4 \cdot 10^{-6}$	0.04
	" well 155		$6 \cdot 10^{-6}$	0.06
Devonian	" well 155 "A"	0.85	$2 \cdot 10^{-6}$	0.02
	" well 12	0.85	$6 \cdot 10^{-6}$	0.06
Cenozoic age	Vvedenovka, well 303/61	0.835	$2 \cdot 10^{-6}$	0.02
	Ishimbai, well 7/19	0.890	none	-
	" well 2/1	0.870	traces	-
	Kartashevka, well 45/45	0.905	$2.5 \cdot 10^{-6}$	0.025
	Kinzebulatovo, well 159	0.90	$6 \cdot 10^{-6}$	0.06
	Kazanovka, well 47	0.874	$4 \cdot 10^{-6}$	0.04
	" well 48	0.868	$3 \cdot 10^{-6}$	0.03
Average germanium content			$4.4 \cdot 10^{-6}$	0.044

analyses are presented in Table 6.

The germanium content in the oils of Tataria ranges from traces to  $10^{-6}\%$ .

The oils from the Suleevo-Tashliyar field and from one of the wells of Abdrrakhman area are distinguished by their high germanium content ( $10^{-5}\%$ ). In other fields germanium content does not exceed  $10^{-6}\%$ . The oils of Tataria are relatively light with specific gravity ranging from 0.84 to 0.88.

There is no relation between specific gravity and germanium content. The average germanium content in all analyzed samples is 0.053 g/ton.

Oils of the Orenburg district. In the Orenburg district oils from Cenozoic, Lower Carboniferous and Devonian beds were investigated. The samples were collected at Pilyugano, Krasnoyarka, Sultangulovo, Zhukovom and Tarkhany fields. The analyses are given in Table 7.

Germanium was found in all samples. Its content varies from 0.02 to 0.06 g/ton. The dependence of germanium content on the geological age of the oils, their specific gravities being almost the same, is rather clear:

Table 6  
Oils of Tataria

Age	Bed	Locality	Sp. G.	Ge content	
				%	g/ton
Devonian	D <sub>1</sub>	Minibaev, well 59	0.86	traces	-
	D <sub>1</sub> <sup>1+2</sup>	Suleevo-Tashliyar, well 66	0.86	1.6 · 10 <sup>-5</sup>	0.16
	D <sub>1</sub>	Bavly, well 15	0.84	1 · 10 <sup>-5</sup>	0.1
	D <sub>1</sub>	" well 1	0.83-0.88	none	-
	D <sub>1</sub>	Abdrakhman, well 32	0.86	none	-
	D <sub>1</sub> <sup>1+2</sup>	" well 716	0.87	1.6 · 10 <sup>-5</sup>	0.16
	D <sub>1</sub> <sup>1</sup>	Aktash, well 572	0.86	4 · 10 <sup>-6</sup>	0.04
	D <sub>1</sub> <sup>0</sup>	Aznakaev, well 536	0.88	4 · 10 <sup>-6</sup>	0.04
	D <sub>1</sub> <sup>0</sup>	" well 538	0.87	6 · 10 <sup>-6</sup>	0.06
	D <sub>1</sub> <sup>1</sup>	" well 543	0.87	4 · 10 <sup>-6</sup>	0.04
	D <sub>1</sub> <sup>1</sup>	Romashkino, well 107		4 · 10 <sup>-6</sup>	0.04
	D <sub>1</sub> <sup>111</sup>	" well 42		2 · 10 <sup>-6</sup>	0.02
	D <sub>1</sub> <sup>111</sup>	Mordovskiy, Aktash, well 88		3 · 10 <sup>-6</sup>	0.03
	D <sub>1</sub> <sup>IV</sup>	Bavly 308	0.83-0.88	4 · 10 <sup>-6</sup>	0.04
		Average germanium content		5.3 · 10 <sup>-6</sup>	0.053

Ge g/ton

Permian oils	0.03
Carboniferous oils	0.073
Devonian oils	0.35

Germanium content is higher in the oldest oils (Devonian) although its absolute content is not high.

The oils of the Kuibyshev district. Several samples of oil from Permian and Carboniferous deposits were analyzed. The results are given in Table 8.

The oils of the district are poor in germanium. Its average content in all investigated samples is 0.03 g/ton. As in the Orenburg district, Permian oils are poorer in germanium than Carboniferous, but this conclusion must be considered tentative because of the small number of analyzed samples.

No germanium was found in the very light Mukhanovsk oil (sp. g. 0.811).

Table 7  
Oils of Orenburg District

Period	Age	Locality	Sp. G.	Ge content	
				%	g/ton
Permian	Kungurian	Pilyugino, well 64	0.87	$3 \cdot 10^{-6}$	0.03
Devonian		Krasnoyarskaya, well 28	0.87	$3.6 \cdot 10^{-5}$	0.36
Permian	Sakmarian	Krasnoyarskaya, well 42	0.86	$2 \cdot 10^{-6}$	0.02
Carboniferous		Krasnoyarskaya, well 40	0.86	$1.2 \cdot 10^{-5}$	0.12
Permian	Tournaisian	Sultangulovo, well 5	0.88	$2 \cdot 10^{-6}$	0.02
Devonian		Sultangulovo, well 100	0.88	$2.6 \cdot 10^{-5}$	0.26
Carboniferous	Tournaisian	Sultangulovo, well 112	0.87	$2 \cdot 10^{-6}$	0.02
Devonian		Sultangulovo, well 106	0.88	$1 \cdot 10^{-5}$	0.10
Permian	Kungurian	Zhukovo, well 1		$4 \cdot 10^{-6}$	0.04
Permian	Ufimian formation	Krasnoyarka, well 22	0.86	$4 \cdot 10^{-6}$	0.04
Carboniferous		Tarkhany, well 120	0.85	$8 \cdot 10^{-6}$	0.08
Devonian		Tarkhany, well 127	0.86	$6.9 \cdot 10^{-5}$	0.69
Average germanium content				$1.5 \cdot 10^{-5}$	0.15

It should be mentioned that in the Kuibyshev district only the oils from left bank fields were analyzed. The oils from the Samarskaya Luka fields were not sampled. It is possible that their germanium content is different, but strong enrichment in germanium can hardly be expected.

#### Summary

1. Germanium was found in the oils of all most important petrolierous provinces of the Soviet Union in the following amounts (average content in

Table 8  
Oils of the Kuibyshev District

Period	Stage, formation	Locality	Sp.G.	Ge content	
				%	g/ton
Permian	Kalinov formation	Stepanovka, well 168	0.87	$2 \cdot 10^{-6}$	0.02
Permian	" "	Stepanovka, well 418	0.87	$4 \cdot 10^{-6}$	0.04
Carboniferous	Tournaisian stage	Kalinovka, well 9		$6 \cdot 10^{-6}$	0.06
Devonian	Bed IV	Mukhanovo, well 68	0.811	none	-
Permian		Yablonya, well 168	0.865	$2 \cdot 10^{-6}$	0.02
Average germanium content				$3 \cdot 10^{-6}$	0.03

grams per ton):

Petroliferous locality	Ge, g/ton
Sakhalin	0.015
Azerbaidzhan	0.063
Fergana	0.034
Bashkiria	0.044
Tataria	0.053
Kuibyshev district	0.033
Orenburg district	0.150

2. The highest germanium content was found in the following oils:

			Ge content g/ton
Azerbaidzhan	Artem Island	PK	0.32
	Kala	Balakhan formation	0.32
Fergana	S. Alamyshak	Sumsarsk and Alai stages	up to 0.26
	Maili-Su		
Tatariya	Suleevo		
Orenburg district	Abdrakhmanovo	Upper Devonian	0.16
	Tarkhany	Upper Devonian	0.69

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Received for publication  
July 22, 1958.

## BEHAVIOR OF TITANIUM DURING THE FORMATION OF SKARNS AT THE TYRNY-AUZ ORE DEPOSIT

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The behavior of titanium during the formation of the Tyrny-Auz skarn ore deposit was touched upon by the author in his account of the behavior of rare and dispersed elements during the process of skarn formation (Nesterenko, Studenikova, and Savinova, 1958). Further study of the deposit and additional data make it possible to consider this question in greater detail.

The skarn body, with a complex zoned structure, was formed at the contact between limestones and biotite hornfelses crumpled into an anticlinal fold. The replacement of the hornblende hornfelses resulted in the formation of pyroxene-garnet skarns and pyroxene and amphibole hornfelses. The last two rocks are called hornfelses only as a matter of convention, mainly because of their structural and textural characteristics. They are typical metasomatic rocks, normal members of the metasomatic series. The skarns formed in the limestones are wollastonite-idocrase, pyroxene and pyroxene-garnet rocks.

The skarns are composed of typical lime minerals. They contain pyroxene (diopside-hedenbergite), garnet (grossularite-andradite), plagioclase (andesine to bytownite), wollastonite, idocrase and amphibole (antinolite). Quartz is present. Fluorite and sphene occur in subordinate amounts.

In analyzing the behavior of titanium during skarn formation, we shall discuss, first, the metasomatic rocks developed after the biotite hornfelses (Table 1).

The nearly bimimetic pyroxene-garnet skarns (earlier than the monomineralic garnet skarns) were formed during the most intensive reworking of biotite hornfelses with additions of high concentrations of iron and calcium by the solutions. The pyroxene, or, more exactly, the pyroxene-plagioclase hornfelses, are fine-grained hornfels-like rocks resulting from a less intensive alteration of biotite hornfelses. Their principal rock-forming minerals are pyroxene and plagioclase. Finally, a study of the amphibole-biotite hornfelses shows that they are products of lime

Distribution of Titanium in Different Types of Metasomatic Rocks  
at the Tymy-Auz Deposit\*

Components	Components	Replaced limestones		Replaced biotite hornfelses			Biotite hornfelses
		Marbles	wollastonite- idocrase skarns	Pyroxene- skarns	Pyroxene- skarns	Pyroxene- hornfelses	
Number of analyses	2	23**		4	4	3	6
Components							
TiO <sub>2</sub>	—	0.03—0.05	0.08	0.22	0.41	0.62	0.88
CaO	53.85	—	23.44	26.77	26.08	13.56	7.12
Fe <sub>2</sub> O <sub>3</sub>	0.22	—	2.86	5.24	5.18	1.23	0.84
FeO	0.25	—	20.70	12.90	9.46	7.35	5.11
Total Fe	0.34	—	18.09	13.69	10.97	6.57	4.66
Fe <sub>2</sub> O <sub>3</sub> /FeO	0.88	—	0.13	0.41	0.54	0.17	0.27

\* In compiling this table analyses by A. D. Kalenov were used as well as the author's data.

Analyses were performed by V. A. Zolotareva, Moscow State University.

\*\* Results of semiquantitative spectrographic analyses.

metasomatism without addition of iron (Table 1).

In the biotite hornfelses, composed of biotite, quartz, feldspars and ilmenite, the groundmass is often replaced at the contact with skarn minerals and potash feldspar, and the biotite, by muscovite. This is explained by the precipitation in the biotite hornfelses of potassium and aluminum actively removed from the zone of replacement during the process of skarn formation.

A study of the distribution of titanium in the skarns and in the enclosing rocks shows that its maximum content is in the biotite hornfelses. Titanium is practically absent from the marbles. In all metamorphosed rocks the titanium content is lower than in the biotite hornfelses (Table 1). During the process of skarn formation titanium was introduced into the metasomatic rocks from the biotite hornfelses. Part of it was dissolved and removed. An examination of Table 1 may give the impression that no titanium was removed, but that it was redistributed and fixed in the skarns formed in the limestones during the replacement of the biotite hornfelses. This conclusion would be incorrect. The limestone skarns constitute not more than 15-20% of the total volume of the skarns. From 80 to 85% of the skarns were formed from replacement of the biotite hornfelses. If it is assumed that titanium was merely redistributed, then its content in the limestone skarns should be several times higher than it actually is. In reality, this is not so. We must consider, therefore, that although titanium was introduced into the limestone skarns, the addition was small. The main mass of titanium during the formation of the skarn ore deposit was carried out in the replacement zones. A comparison of its content in the different types of metamorphosed rocks shows a direct connection between the removal of titanium and the intensity of the replacement of the biotite hornfelses by skarn. The pyroxene-garnet skarns have the lowest titanium content, but it increases regularly as the degree of metamorphism of the biotite hornfelses decreases (pyroxene and amphibole-biotite hornfelses).

Let us examine systematically the behavior of titanium in the different types of metamorphosed rocks. Khrushchov (1958) noted that in the biotite hornfelses of Tyrny-Auz, titanium enters into biotite, and when the latter decomposes, titanium is released as sagenitic rutile. Biotite is a carrier and concentrator of a whole series of rare and dispersed elements, including titanium (Mateev, 1937; Rankama and Sahama, 1949; Dmitriev and Znamenskii, 1956). In our locality it contains 1.72%  $TiO_2$ . However, in the biotite hornfelses of Tyrny-Auz, titanium is not restricted to biotite. An examination of polished sections shows that the opaque mineral in the hornfelses is almost wholly ilmenite (96-98%). Magnetite is present in very small amounts. To confirm optical identification of ilmenite, the heavy fraction was separated from the biotite hornfelses and analyzed, and was found to contain over 20%  $TiO_2$ . An x-ray diffraction analysis of a sample containing 40-50% of the heavy fraction also showed that its main component was ilmenite.

The most widespread varieties of biotite hornfelses contain 30 to 40% biotite and 0.5 to 1% ilmenite. The distribution of titanium in rocks of this composition shows that, in spite of its preferred association with biotite (65%), 30% of all titanium in the biotite hornfelses occurs in ilmenite (Table 2).

It should be noted that the content of these two minerals in the hornfelses is variable. Therefore, if the content of biotite is low and that of ilmenite high, the greater part of the titanium in the rocks may be fixed in the ilmenite.

During the muscovitization of biotite at the contacts between skarns and

Table 2

Distribution of Titanium in Biotite Hornfelses  
(sample No. 0180)

Minerals	Content of mineral in rock, (wgt. %)	Content of $TiO_2$ in mineral, % (wgt. %)	Amount of $TiO_2$ contributed by mineral to rock (in PPM)	Amount of $TiO_2$ contributed to the rock by the mineral, %	Total $TiO_2$ content in rock, (in PPM)
Biotite*	33.50	1.72*	0.57	65	
Ilmenite	0.50	52.60	0.26	30	
Total			0.81	95	8.70*

\*Yu. B. Kholina, analyst

In biotite hornfelses, titanium separated and formed yellow grains of rutile. Ilmenite, at this time, did not undergo a noticeable alteration, but as soon as the amphibole (actinolite) appeared in the hornfelses, indicating the introduction of calcium, fine-grained sphene began to develop at the expense of ilmenite. Occasionally sphene occurs as rims on ilmenite, but more frequently it replaces ilmenite completely. In one form or another, this phenomenon is characteristic of all amphibole-biotite hornfelses. As for the newly formed rutile, it was partially preserved during the introduction of calcium together with the incompletely decomposed flakes of biotite. The formation of pyroxene hornfelses was accompanied by the final replacement of ilmenite and rutile with the formation of poorly crystallized nodular sphene.

The decomposition of the iron-bearing minerals, ilmenite and biotite, during the replacement of the biotite hornfelses was not accompanied by the formation of magnetite in association with sphene. This was due, evidently, to calcium being in excess of iron during the skarn forming processes caused by the fixation of all iron in the silicates of the amphibole-biotite and pyroxene hornfelses. The reducing environment in which the replacement of the biotite hornfelses occurred must also have had an effect. Especially instructive in this respect are the amphibole-biotite hornfelses. It was mentioned earlier that they were formed without introduction of iron, as indicated by practically the same iron content in both the biotite and the amphibole-biotite hornfelses. But the ferric/ferrous ratio in the latter is less than in the biotite hornfelses, and this indicates that iron was partly reduced in the amphibole-biotite hornfelses. An analogous  $Fe_2O_3/FeO$  ratio is found also in the pyroxene hornfelses, although iron was obviously added in this case (Table 1). The reducing environment in the amphibole-biotite and pyroxene hornfelses may be one of the factors which prevented the formation of magnetite (not to mention hematite), because the decomposition of ilmenite and biotite would yield mainly ferrous iron, which would

readily combine with calcium to form either actinolite (in the amphibole-biotite hornfelses) or pyroxene (in pyroxene hornfelses).

The distribution of sphene through the masses of amphibole-biotite and pyroxene hornfelses is, on the whole, uniform. In some cases, however, in the pyroxene hornfelses, it is grouped into chains, evidently localized in microscopic fractures, or occurs in large amounts in the plagioclase and quartz-plagioclase veinlets. These examples show how titanium was removed from the pyroxene hornfelses. Its removal into the quartz-plagioclase veinlets evidently played a very important role during the formation of pyroxene-garnet hornfelses as well and was the decisive factor in the impoverishment of the skarns in titanium.

The pyroxene-garnet skarns were formed by recrystallization of pyroxene hornfelses under the action of solutions highly enriched in calcium and iron. This process was accompanied by decomposition of the nodular grains of sphene characteristic of the pyroxene hornfelses and removal of a considerable quantity of titanium from the zone of skarn formation. The remaining sphene formed euhedral wedge-shaped crystals during the process of recrystallization. As a rule, sphene occurs relatively infrequently in the skarns themselves. On the other hand, it is sometimes found in rather large amounts in quartz-plagioclase and very rarely in calcite veinlets. The active removal of titanium by solutions, which began as early as the time of formation pyroxene hornfelses, led to a considerable decrease in the titanium content in skarns as compared with biotite hornfelses (Table 1).

As mentioned above, titanium was introduced in small amounts into skarns developed in limestones. Sphene is rare but occasionally occurs in them. It was found even in the wollastonite-idocrase skarns of the outer replacement zone. The occurrence of sphene here is incidental and does not contradict the existing idea of its absence from the skarns replacing limestones.

Besides types of metasomatic rocks already discussed, the deposit contains one more variety, the pyroxene-plagioclase skarns. These rocks resemble pyroxene hornfelses, but are limited in distribution, being found mainly at the contact between skarns and biotite hornfelses. The origin of the pyroxene-plagioclase skarns is still unknown; therefore, without making any statements concerning their genetic characteristics, it will be noted, merely, that they have high titanium content (0.76%  $TiO_2$ , according to one determination).

In the replacement of biotite hornfelses with the formation of different types of skarns, titanium not only is fixed in sphene, but enters into the lattices of the skarn minerals. Spectrographic analysis of monomineralic fractions shows that its maximum content is in the minerals containing aluminum, such as garnet and idocrase (Table 3). This suggests that in these minerals titanium replaces aluminum by ionic substitution. The presence of titanium in the pyroxene, which according to the chemical analyses contains no aluminum, and in wollastonite indicates the possibility of replacement of silicon by the tetravalent titanium (Rankama and Sahama, 1949; Fersman, 1939). However, its very low content in these minerals shows that this diadochy, if it occurs at all, is very limited.

Computations show that the titanium fixed in the crystal lattices of silicates of the pyroxene-garnet skarns amounts to only 15-20% of the total titanium in the rock. As compared with biotite hornfelses, in which 65% of the titanium is fixed in biotite, its amount occurring in ionic substitution in silicates of the pyroxene-garnet skarns is small. The bulk of the titanium in these skarns is in sphene (80-85%).

Table 3

Distribution of Titanium in the Skarn Minerals  
of the Tyrny-Auz Deposit

Minerals	Spectrographic analyses		Chemical analyses*	
	Number of analyses	Average $TiO_2$ content (wgt. %)	Number of analyses	Average $TiO_2$ content (wgt. %)
Pyroxene (salite)	15	0.01	2	Traces
Garnet (grossularite-andradite)	26	0.15	5	0.14
Sillastone	15	0.003	-	-
Schist	13	0.5	1	0.54

After A. D. Kalenov (1948) and S. P. Solov'ev (1940).

Data on the distribution of titanium and mode of its occurrence in the country rocks and in products of their replacement at the Tyrny-Auz deposit may be summarized as follows:

1. During the process of skarn formation in marbles and biotite hornfelses, no titanium was introduced by solutions; it was contributed to the skarns by biotite hornfelses undergoing replacement. In the latter, it occurs not only in biotite but also in ilmenite. In the metasomatic rocks, titanium becomes fixed in sphene.
2. The replacement of biotite hornfelses is accompanied by a partial removal of titanium into the plagioclase and quartz-plagioclase veinlets characteristic of pyroxene hornfelses and pyroxene-garnet skarns.
3. Besides entering into ilmenite and sphene, titanium ionically substitutes for aluminum and possibly for silicon in a number of other minerals.

The author expresses his gratitude to V. V. Shcherbina for advice and in this work; and to V. A. Zolotareva, V. V. Korolev, K. I. Tobelko and B. Kholina, who undertook to make chemical, spectrographic and x-ray diffraction analyses.

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Received for publication  
November 13, 1958.

## THE $U^{234}/U^{238}$ RATIO IN SOME SECONDARY MINERALS

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The deviation of the isotopic constitution of uranium from the normal, as far as the content of the two genetically related isotopes,  $U^{238}$  and  $U^{234}$ , concerned, was first discovered by V. V. Cherdynsev and P. I. Chalov in 1953 during an investigation of the  $U^{234}/U^{238}$  ratio in a number of secondary minerals, in ground waters and in extracts from minerals. The method developed in this investigation [2] permitted determination of the  $U^{234}/U^{238}$  ratio in weakly active samples with required accuracy only by subtracted measurement of alpha and especially beta activities of the samples. Nevertheless, the existence of isotopic shift towards relative enrichment of some samples of natural waters and extracts from minerals in  $U^{234}$  was proved beyond the shadow of a doubt, because the isotope ratio in these cases deviated considerably from the normal ( $U^{234}/U^{238} = 1$ ), ranging from 1.5 to 8. I. E. Starik, F. E. Starik and B. A. Mikhailov [3] refined the method of measuring the  $U^{234}/U^{238}$  ratio and produced isotope shift in uranium under laboratory conditions by leaching and sublimation. Using a more precise method of determining the  $U^{234}/U^{238}$  ratio from the alpha-particle spectra of radiochemically pure uranium samples, V. I. Baranov, A. Surkov and V. D. Vilenskii [4] also observed isotope shift produced in the laboratory by leaching.

Resuming the investigations begun earlier, the author determined the  $U^{234}/U^{238}$  ratio in minerals collected from the zones of oxidation and secondary enrichment of an ore deposit. The results of this work are here presented.

The minerals selected for study were separated from the enclosing rocks decomposed by acids. To obtain radiochemically pure samples, uranium was separated from other radioactive elements and electrodeposited in thin film on copper discs. The procedure was described in reference [1] and will not be discussed here.

The  $U^{234}/U^{238}$  ratio was determined by the method previously developed by the author [2], which consists of comparing the alpha and beta activities of radiochemically pure samples with those of a standard prepared from uraninite. In the determination of the  $U^{234}/U^{238}$  ratio by this method, alpha activity is the measure of the sum of the isotopes  $U^{234}$  and  $U^{238}$  and beta activity, the measure of the  $U^{238}$  content, provided the presence in the sample of the weakly radioactive isotope  $U^{236}$  and the product of its

decay,  $UY$ , is neglected. The formula derived by the author for the determination of the  $U^{234}/U^{238}$  ratio [2] takes the presence of  $U^{235}$  into account, but this is necessary only when the error in the determination of the alpha and beta activities of the samples is small.

The alpha activity of the samples was measured on an infinitely thin film of uranium with apparatus DA, and beta activity was measured on apparatus B-2 with counter AC-2.

Inasmuch as the knowledge of the error of measurement is very important in the evaluation of isotope shift, the method of computing the error involved in the determination of the isotopic composition of uranium by the measurement of alpha beta activities will be briefly discussed.

The formula derived by the author [2] for the determination of the isotopic composition of uranium from the alpha and beta activity measurements on radiochemically pure samples of uranium in its simplest form (without correction for  $U^{235}$  and with the assumption that equilibrium exists between  $UX_1$  and  $U^{238}$  after the separation of radiochemically pure uranium) can be written as follows:

$$\frac{U^{234}}{U^{238}} = k = 2 \frac{\alpha \cdot \beta_0}{\alpha_0 \cdot \beta} - 1, \quad (1)$$

where  $\alpha$  and  $\alpha_0$  are the alpha activities of the sample and the standard at equilibrium in counts per minute, and  $\beta$  and  $\beta_0$  are beta activities of the sample and standard.

Expression (1) may be written also in the form:

$$k = 2 \frac{(\alpha_s - \alpha_b)(\beta_r - \beta_b)}{(\alpha_r - \alpha_b)(\beta_s - \beta_b)} - 1, \quad (2)$$

where  $\alpha_s$  and  $\alpha_r$  are alpha activities of sample and standard, the background being disregarded,

$\alpha_b$  -- background during the measurement of alpha activity,

$\beta_s$  and  $\beta_r$  -- beta activities of sample and standard without subtraction of the background, and

$\beta_b$  -- background during the measurement of beta activity.

Since  $\alpha_b$  (1 to 2 counts/min) is usually ten times and in most cases a hundred times smaller than  $\alpha_s$  and  $\alpha_r$ , it may be considered that:

$$\alpha_s - \alpha_b \approx \alpha_s$$

$$\alpha_r - \alpha_b \approx \alpha_r$$

Introducing this assumption into expression (2), we have:

$$k = 2 \frac{\alpha_s (\beta_r - \beta_b)}{\alpha_r (\beta_s - \beta_b)} - 1. \quad (3)$$

Using equation (3), the standard deviation of the value of  $k$ , due to the statistical character of radioactive decay may be written:

$$\sigma = \sqrt{\left(\frac{\partial k}{\partial \alpha_s} \Delta \alpha_s\right)^2 + \left(\frac{\partial k}{\partial \beta_r} \Delta \beta_r\right)^2 + \left(\frac{\partial k}{\partial \beta_b} \Delta \beta_b\right)^2 + \left(\frac{\partial k}{\partial \alpha_r} \Delta \alpha_r\right)^2 + \left(\frac{\partial k}{\partial \beta_s} \Delta \beta_s\right)^2}, \quad (4)$$

where  $\Delta \alpha_s = \sqrt{\frac{\alpha_s}{t_s}}$ ,  $\Delta \beta_r = \sqrt{\frac{\beta_r}{t_r}}$ ,  $\Delta \beta_b = \sqrt{\frac{\beta_b}{t_b}}$ ,  $\Delta \alpha_r = \sqrt{\frac{\alpha_r}{t_r}}$ ,  $\Delta \beta_s = \sqrt{\frac{\beta_s}{t_s}}$

and  $t$  is the duration of the measurements.

Differentiating (3) and substituting the partial derivatives in (4), we obtain:

$$\sigma = \frac{2}{\alpha_r(\beta_s - \beta_b)} \sqrt{[(\beta_r - \beta_b) \Delta \alpha_s]^2 + [\alpha_s \Delta \beta_r]^2 + \left[\alpha_s \frac{\beta_r - \beta_s}{\beta_s - \beta_b} \Delta \beta_b\right]^2 + \left[\frac{\alpha_s(\beta_r - \beta_b)}{\alpha_r} \Delta \alpha_r\right]^2 + \left[\alpha_s \frac{\beta_r - \beta_b}{\beta_s - \beta_b} \Delta \beta_s\right]^2}. \quad (5)$$

Having determined  $\sigma$  for each measurement of  $k$  and the weights corresponding to each measurement from expression  $\frac{\sigma_1^2}{\sigma_2^2} = \frac{\omega_2}{\omega_1}$  (for example [5, 6]), we find the mean value  $\bar{k}$  and the probable errors  $p_{\bar{k}}$  for a series of measurements by the formulas:

$$\bar{k} = \frac{\sum \omega_k}{\sum \omega}, \quad p_{\bar{k}} = 0.67 \sigma_{\bar{k}}, \quad (6)$$

where  $\sigma_{\bar{k}}$  is the standard deviation of the series of measurements. Having obtained the mean values  $\bar{k}$  and the probable error  $p_{\bar{k}}$  in their determination for each target, we find the general mean value  $\bar{\bar{k}}$  and its probable deviation  $p_{\bar{\bar{k}}}$  by the expressions:

$$\bar{\bar{k}} = \frac{\sum (\bar{k} m^2 / p_{\bar{k}}^2)}{\sum m^2 p_{\bar{k}}^2}, \quad p_{\bar{\bar{k}}} = \sqrt{\frac{1}{\sum \frac{1}{p_{\bar{k}}^2}}}, \quad (7)$$

where  $m$  is a constant (probable deviation of the mean value whose weight is unity).

As an illustration we present in Table 1 the initial data and the results of calculation of  $\bar{k}$  (and  $p_{\bar{k}}$ ) for a sample of redeposited pitchblende (No. 17, Table 2).

A brief description of the samples used in the investigation and their U<sup>234</sup>/U<sup>238</sup> ratios are given in Table 2.

The U<sup>234</sup>/U<sup>238</sup> ratio was determined in forty-four samples of minerals, and at least two discs with an infinitely thin uranium film were prepared for each mineral.

The average values of the U<sup>234</sup>/U<sup>238</sup> ratio for each mineral obtained on the basis of three or four measurements of parallel samples, and the error in their determination, are presented in Table 2.

Table 2 shows that the disturbance of isotopic equilibrium in the investigated minerals occurs in some cases only. Of the forty four samples, only

Table 1

Initial Data and the Results of Recalculation of  $\underline{k}$  and  $p_k$  for a Sample of Redeposited Pitchblend (17)

Measurements	$\alpha_S = x$	$\alpha_R = \alpha_0$	First target				Second target			
			$\Delta\alpha_S^2$	$\Delta\alpha_R^2$	$\beta_S$	$\beta_R$	$\beta_B$	$\Delta\beta_S^2$	$\Delta\beta_R^2$	$\Delta\beta_B^2$
1st measurement	145	98	29	19,6	114	103	64	22,8	20,6	12,8
	146	100	29,2	20	106	96	61	17,7	16	10,2
	150	100	30	20	105	94	59	21	18,8	11,8
$\bar{k}_1 = 1,29$										
$\bar{p}_{\bar{k}_1} = 0,15$										
1st measurement	106	98	33,2	19,6	117	99	63	19,5	16,5	10,5
	172	100	34,4	20	115	97	60	19,2	16,2	10
	173	99	34,6	19,8	115	97	59	13,9	13,9	8,4
$\bar{k}_2 = 1,32$										
$\bar{p}_{\bar{k}_2} = 0,13$										
$\bar{k}$	$\bar{k} = 1,31$									
	$\bar{p}_{\bar{k}} = 0,10$									

Note: Comma represents decimal point.

Table 2

The U<sup>234</sup>/U<sup>238</sup> Ratio in Some Secondary Minerals

Sample No.	Brief description of sample	U <sup>234</sup> /U <sup>238</sup>
	Oxidized zone	
1	Autunite on altered granite porphyry	0.67+0.07
2	Powdery autunite on altered granite porphyry	0.87+0.09
3	Autunite on quartz	0.84+0.09
4	Torbernite on altered granite porphyry	0.97+0.10
5	Torbernite on strongly silicified granite porphyry	0.92+0.09
6	Torbernite on altered granite porphyry	1.03+0.07
7	Torbernite in quartz-barite vein	0.95+0.07
8	Torbernite on altered granite porphyry	0.98+0.06
9	" " " "	1.02+0.09
10	Zeunerite on altered granite porphyry	0.95+0.07
11	Residual pitchblende on a barite vein	0.56+0.08
12	Torbernite on granite porphyry	1.00+0.06
	Oxidized subzone of the zone of cementation	
13	Schroeckingerite on granodiorite	1.04+0.05
14	" "	1.05+0.07
15	Residual pitchblende on quartz	0.94+0.07
16	Redeposited pitchblende on quartz	1.12+0.07
17	Redeposited pitchblende on chloritized granite porphyry	1.31+0.10
18	Residual pitchblende on strongly chloritized granite porphyry	0.95+0.07
19	Residual pitchblende on altered granite porphyry	0.95+0.07
20	Redeposited pitchblende on altered granite porphyry	1.06+0.10
21	Redeposited pitchblende on quartz	1.01+0.05
22	Redeposited pitchblende on granite porphyry	1.11+0.10
	Zone of cementation	
23	Redeposited pitchblende on quartz-ankerite veinlet	1.04+0.05
24	Redeposited pitchblende on quartz	1.10+0.08
25	Redeposited pitchblende on silicified granite porphyry	0.95+0.07
26	Redeposited pitchblende on granite porphyry	0.87+0.09
27	Redeposited pitchblende on strongly pyritized andesite	0.96+0.08
28	Residual pitchblende on granite porphyry	0.85+0.10
29	Redeposited pitchblende on quartz	0.98+0.05
30	Redeposited pitchblende on andesite	1.06+0.07
31	Redeposited pitchblende on altered granite porphyry	1.06+0.07

Table 2 (Cont'd.)

The  $U^{234}/U^{238}$  Ratio in Some Secondary Minerals

Sample No.	Brief description of sample	$U^{234}/U^{238}$
32	Redeposited pitchblende with sulfates	$0.99 \pm 0.09$
33	Barite vein with a crust of redeposited pitchblende	$0.98 \pm 0.10$
34	Residual pitchblende on altered granite porphyry	$0.85 \pm 0.10$
35	Residual pitchblende on altered granite porphyry	$0.78 \pm 0.08$
36	Residual pitchblende on altered granodiorite	$0.86 \pm 0.10$
37	Redeposited pitchblende on altered granodiorite	$1.08 \pm 0.06$
38	Redeposited pitchblende on quartz-barite vein	$1.16 \pm 0.10$
39	Residual pitchblende on granite porphyry	$0.97 \pm 0.07$
40	Residual pitchblende on altered granite porphyry	$1.01 \pm 0.07$
41	Residual pitchblende on quartz-chlorite-sulfide vein	$1.03 \pm 0.07$
42	Residual pitchblende on chloritized granite porphyry	$0.87 \pm 0.07$
43	Residual pitchblende on granodiorite	$0.95 \pm 0.08$
44	Uraninite on granodiorite	$0.97 \pm 0.07$

four gave obviously anomalous isotope ratios (Nos. 1, 11, 17 and 35); in all other cases it is difficult to be certain that the isotope ratios are anomalous, because the error of measurement does not permit a unique solution, but there appears to be a tendency in the residual pitchblendes towards a decrease in the  $U^{234}/U^{238}$  ratio as compared with the normal.

To check the method of determination of the  $U^{234}/U^{238}$  ratio by means of alpha-beta measurements and verify the obtained data, the isotopic constitution of uranium in several samples was determined from their alpha-particle spectra in the Research Laboratory of Experimental Physics at the Kazakh State University on a multichannel analyzer. The results of this work are given in Table 3. The same table gives for comparison the results of determination of the  $U^{234}/U^{238}$  ratio by the author's method.

The last two columns of Table 3 show that the multichannel analyzer gives more accurate results; however the method of determination of the  $U^{234}/U^{238}$  ratio by comparing alpha and beta radiation from radiochemically pure samples of uranium with the equilibrium standard ( $U^{234}/U^{238} = 1$ ) also gives good results but with a greater error of measurement.

The data presented above indicate that in naturally occurring substances, and in uranium minerals in particular, isotope equilibrium may shift not only towards relative enrichment in  $U^{234}$  but also towards impoverishment in  $U^{234}$ . As a result of differential leaching of one isotope ( $U^{234}$ ), the

Table 3

The U<sup>234</sup>/U<sup>238</sup> ratios Determined by the Analysis  
of the Alpha Particle Spectra and by Comparison of Alpha-  
and Beta-Radiations from the Samples  
and from an Equilibrium Standard

Sample No. in Table 2	Description of sample	U <sup>234</sup> /U <sup>238</sup>	
		by alpha particle spectrum	by comparison of alpha- and beta radiations from the sample and the equilib- rium standard
1	Autunite on altered granite porphyry	0.62 $\pm$ 0.04	0.67 $\pm$ 0.07
27	Powdery autunite on altered granite porphyry	0.92 $\pm$ 0.04	0.87 $\pm$ 0.09
10	Zeunerite on altered granite porphyry	0.94 $\pm$ 0.05	0.95 $\pm$ 0.07
11	Residual pitchblende on barite vein	0.68 $\pm$ 0.04	0.56 $\pm$ 0.08
17	Redeposited pitchblende on chloritized granite porphyry	1.29 $\pm$ 0.05	1.31 $\pm$ 0.10
34	Residual pitchblende on altered granite porphyry	0.88 $\pm$ 0.08	0.85 $\pm$ 0.10

Isotope equilibrium becomes so disturbed that the disturbance can be established by the simplest methods. Undoubtedly the basic role in the process of separation of genetically related uranium isotopes under natural conditions is played by radioactivity as a result of which U<sup>234</sup> becomes weakly bonded or not bonded at all in the crystal lattices of minerals. However, in the case of minerals in which uranium is present in the tetravalent state, an equally important role is played by the process of oxidation, for the isotope which is free or only weakly bonded in the lattice oxidizes much more easily to the hexavalent state, in which it is readily transported by circulating solutions.

It may be said in summary that the author succeeded in demonstrating that the equilibrium between U<sup>234</sup> and U<sup>238</sup> may be shifted under natural conditions towards relative impoverishment of the minerals in U<sup>234</sup>, the effect being analogous to that produced by V. I. Baranov, Yu. A. Surkov and V. D. Vilenskii under laboratory conditions.

The author expresses deep gratitude to the chairman of the Department of Experimental Physics, Kazakh State University, and Professor V. V. Cherdynsev for checking the data on the isotopic ratios in six samples with the multichannel analyzer of the departmental Research Laboratory.

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Received for publication  
October 6, 1958.

## GEOCHEMICAL CHARACTERISTICS OF ALTERATION OF LUDWIGITE ORES

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The ludwigite ores in all magnesium-iron borate deposits of the Soviet Union have been altered by both deuterian and supergene processes; this is especially clearly shown by the Zheleznyi Kryazh deposit in Eastern Transbaikalia.

The Zheleznyi Kryazh deposit lies at the contact between the Lower Paleozoic sedimentary rocks of the Altacha formation and the Kutomar intrusion of Variscan granitoids. Within the mineralized area there are iron and magnesia skarns containing bedded and lenticular bodies of magnetite. The borate mineralization is represented by ludwigite ores genetically related to the magnesian exoskarns and formed by metasomatic replacement of dolomites. There are two types of ore: magnetite-ludwigite and pyrrhotite-ludwigite. The two types differ not only mineralogically but also in the character of the alteration. The primary borates at the locality are magnesioludwigite  $2(\text{Fe}^{2+}, \text{Mg})\text{O} \cdot \text{Fe}^{3+}\text{BO}_3$  and small amounts of warwickite,  $(\text{Mg}, \text{Fe}^{2+})_3\text{TiB}_2\text{O}_8$ , associated with forsterite, magnetite, and the sulfides--pyrrhotite, pyrite and chalcopyrite.

The ludwigite ores were intensively altered by post-depositional processes, both deuterian and supergene.

Deuterian processes caused intensive ascharitization of ludwigite and subsequent replacement of ascharite by the later gangue minerals, serpentine, calcite and others. In the zone of oxidation, ascharite was replaced by hydrous iron oxides and carbonatized. The replacement of the borates is characterized by certain regularities.

As has already been mentioned, the Zheleznyi Kryazh deposit contains magnetite-bearing and sulfide-bearing ludwigite ores. During the process of ascharitization, the replacement of ludwigite in the sulfide-free ores is accompanied by the formation of pseudomorphs after ludwigite composed of aggregates of fine-grained ascharite, magnetite and some hematite (Figs. 1 and 2). Ascharite was deposited in the interstices of the euhedral (secondary) magnetite developed from ludwigite and among the grains of primary magnetite. In the sulfide-bearing ludwigite ores, ludwigite was replaced by ascharite and magnetite, the former developing directly within the ludwigite grains and the latter replacing the sulfides (pyrrhotite and pyrite) near the ludwigite crystals and forming replacement

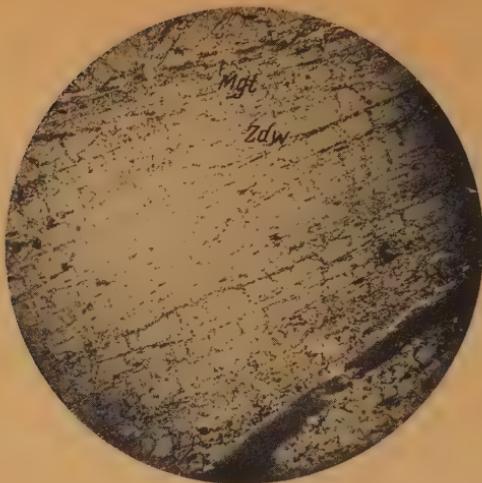


Fig. 1. Ludwigite crystals in the initial stage of ascharitization of magnetite-ludwigite ores.

Polished section. X72 (ludwigite Ldw -- gray, magnetite Mgt -- white, ascharite Ash -- black)



Fig. 2. Completely ascharitized ludwigite. Polished section. X72 (magnetite Mgt -- white, ascharite Ash -- black)



Fig. 3. Pyrrhotite-ludwigite in the initial stage of ascharitization. Polished section. X72 (ludwigite Ldw -- dark gray, pyrrhotite Pyr -- white, ascharite Ash -- black, magnetite Mgt -- gray)



Fig. 4. Completely ascharitized ludwigite in pyrrhotite. Polished section. X72 (ascharite Ash -- black, magnetite Mgt -- gray, pyrrhotite Pyr -- white)

loops and rims (Figs. 3 and 4).

Variation in spatial distribution of the secondary minerals depends on the composition of the primary ludwigite ores: the ascharitized magnetite-ludwigite ores preserve the characteristic radiated structure of ludwigite aggregates, while the ascharitized sulfide-bearing ores are soot-black earthy masses without the primary radiated structure.

Ascharitization of ludwigite is a deuterio process effected by weakly alkaline carbonate solutions at a temperature of about 150°C [1]. The formation of ascharite after ludwigite is not a supergene process as was erroneously stated by I. A. Efimov [2]. This is confirmed by A. D. Keshan [3], who points out that "boric acid is very weak and at room temperature is displaced from the borates even by such a weak acid as the carbonic; at high temperatures, however, because of its lower volatility, boric acid displaces not only carbonic but even stronger acids from their salts." During the high temperature metasomatic processes, orthoborates are stable. In our case, ludwigite and warwickite formed at the expense of dolomite, while during the later low temperature stages of deuterio alteration the orthoborates are replaced by metaborates, i. e., ludwigite by ascharite --  $Mg_2B_2O_5 \cdot H_2O$ .

It has already been pointed out that the secondary minerals of the sulfide-bearing ludwigite ores are distinctive in character. It should be mentioned that in the analogous ores of South Yakutiya the sulfides are not replaced by magnetite during ascharitization, and as a result the secondary minerals formed after ludwigite have identical spatial distribution with magnetite in both types of ore.

Inasmuch as the replacement of sulfides by magnetite in the ludwigite ores of the Zhelezhyi Kryazh deposit and of other similar deposits of Eastern Transbaikalia occurred only near the ludwigite aggregates and was not, therefore, due to increase in the oxidation potential, this phenomenon is most likely due to the difference in the chemical composition between the Southern Yakutiya and Eastern Transbaikaliya ludwigites (Table 1).

The chemical analyses of Yakutian ludwigite given in the table show that it is richer in iron than the Transbaikalian ludwigite. The diadochic substitution of ferrous iron for magnesium has a wide range. Mineralogical studies and experiments with artificial ascharitization of ludwigite [1] show that ludwigite is replaced without noticeable addition or removal of its constituent elements. This suggests that the magnesium and boron of ludwigite go into the making of ascharite, while ferrous and ferric iron contribute to the formation of magnetite and, in part, of hematite. Which of the iron oxides forms from ludwigite is determined by the  $FeO : Fe_2O_3$  ratio, which is 1:2.22 in magnetite. Therefore, if the  $FeO : Fe_2O_3$  ratio in ludwigite is higher than in magnetite, as, for example, in the ludwigite of the Yakutian deposits, then ferrous iron is in excess of ferric and only magnetite will form during ascharitization. In this case, the process of ascharitization may be represented as follows:



ludwigite

ascharite

magnetite

If the ratio is lower than in magnetite, there is a considerable excess of  $Fe_2O_3$  over  $FeO$ , and both magnetite and hematite form as secondary minerals after ludwigite, as, for example, in the deposits of Eastern Transbaikaliya. This also explains the replacement of pyrrhotite and pyrite by

## Chemical Analyses of Ludwomite

Components and main ratios	Ludwomite localities				
	Dogdo River, Yakutiya [4]	Taezhnoe, Yakutiya [5]	Zheleznyi Kryazh, E. Transbaikaliya*	Dono, E. Transbaikaliya [6]	"Zapadnoe", E. Transbaikaliya*
MgO	13,89	22,47	31,95	31,86	33,97
CaO	0,87	—	—	1,07	—
FeO	28,8	23,14	16,32	11,57	5,14
MnO	0,20	0,20	—	—	—
Fe <sub>2</sub> O <sub>3</sub>	38,3	36,87	36,71	36,25	43,05
Al <sub>2</sub> O <sub>3</sub>	—	1,68	—	0,94	0,94
B <sub>2</sub> O <sub>3</sub>	13,55	15,64	15,57	16,16	16,40
TiO <sub>2</sub>	0,24	—	not determ.	—	not determ.
SiO <sub>2</sub>	0,35	—	—	0,31	—
H <sub>2</sub> O-	0,07	—	—	—	—
others	3,24	—	—	1,29	—
Total	99,92	100,00	100,55	99,39	99,67
FeO:MgO	1:0,48	1:0,97	1:1,95	1:2,75	1:6,66
FeO:Fe <sub>2</sub> O <sub>3</sub>	1:1,32	1:1,60	1:2,26	1:3,13	1:8,42

\* Chemical analyses of ludwomite were made by N. N. Deryugina, Associate of the Institute of Geochemistry and Analytical Chemistry, Acad. Sci. USSR.

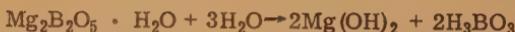
Note: Comma represents decimal point.

magnetite during the ascharitization of sulfide-bearing ludwigite ores, because the sulfides in the deposits of Eastern Transbaikaliya serve as the source of ferrous iron which, compensating for the excess of ferric iron in the strongly magnesian ludwigite, leads to the fixation of all ferric iron in magnetite. The sulfides of the Yakutian ferroludwigite deposits do not undergo any alteration during its ascharitization.

In the succeeding hydrothermal stages, at the Zheleznyi Kryazh deposit, ascharite undergoes intensive replacement by a series of minerals, first of all by serpentine (antigorite) and magnesian chlorite of the leichtenbergite type with the formation of pseudomorphs of these minerals after ascharite and simultaneous removal of boron. The serpentization of ascharite occurred also at the "Zapadnoe" deposit, but on a much smaller scale.

The intensive serpentization affects not only ascharite but also magnesian silicates (forsterite, diopside and others) in the ore-bearing skarns, and this indicates that the process of serpentization is of considerable duration, being syngenetic both with ascharitization and with the process of replacement of ascharite.

Somewhat later than the replacement of ascharite by serpentine, and occurring at still lower temperature, is the replacement of ascharite by brucite and the carbonatization of ascharite. This is another confirmation of the fact that boric acid is easily displaced from its compounds at low temperatures. The decomposition of ascharite with the formation of brucite may be regarded as hydrolysis of ascharite with the liberation of boric acid:



ascharite

brucite

The carbonatization of ascharite is accompanied by formation of calcite and free boric acid. This process is observed not only at the Zheleznyi Kryazh deposit but also at the ludwigite deposits of Verkhnii Uchulen and Argysh-Tag in Gornaya Shoriya.

The ascharitized ludwigite ores in which ascharite is completely replaced by the minerals just described are not changed in appearance but are completely devoid of boron. An example of such ores at the Zheleznyi Kryazh deposit are the radiated structures macroscopically represented by magnetite and the soot-black earthy masses of fine-grained magnetite with an admixture of gangue minerals.

Approximately contemporaneously with the replacement of ascharite by the gangue minerals, the fractures cutting the lime skarns in the vicinity of the borate bodies become filled with vein material composed of calcite, zeolites, prehnite and a certain amount of datolite-- $\text{Ca}_2[\text{BSiO}_4]_2 \cdot (\text{OH})_2$ . It is possible that the formation of datolite is related to the removal of boron during the replacement of ascharite. This hypothesis is supported by the association of datolite with low temperature assemblage of minerals, by the nearness of datolite to the borate deposits (5-10 meters) and by its absence from the lime skarns containing boron-free iron ores. The formation of veinlets terminates the process of formation of deuteritic minerals.

The Zheleznyi Kryazh deposit is characterized by a well developed oxidized zone in the ludwigite ores. Under the action of supergene solutions, both the ludwigite and ascharite ores undergo considerable alteration. The presence of sulfides in the ludwigite ore hastens the oxidation of ludwigite. Investigations show that neither ludwigite nor ascharite is stable in the zone

oxidation.

In the oxidized zone, ludwigite is intensively replaced by hydrous iron oxides which exhibit a dehydration sequence and change in composition from hydrogoethite to hydrohematite, making it possible to establish three stages of the replacement process. The initial stage is the replacement of ludwigite by amorphous hydrogoethite with the formation of replacement structures and preservation of at least a few relict grains of ludwigite. In the next stage, ludwigite is completely replaced by colloform hydrous iron, goethite. During the final stage the hydrous iron oxides developing after ludwigite become strongly dehydrated; they are cryptocrystalline and have the composition of hydrohematite, the most abundant mineral in the oxidized zone of the deposit. The hydrous iron oxides preserve the structure and texture of ludwigite aggregates.

The characteristic feature of the hydrous iron oxides formed after ludwigite is the presence in them of boron due to their high adsorptive capacity, especially for anions [7].

In the monominerotic goethite, the boron content is due to its adsorptive capacity only, and ranges from 1 to 3%  $B_2O_3$ \*. Boron is usually absent from hydrohematite or is present in traces. In an intermediate variety, with near hydrohematite in composition, the boron anhydride content of 38% was found in one case.

It should be noted that the gradual diminution of boron content goes hand in hand with increasing crystallinity of the hydrous iron oxides, i.e., with the change in the structure of their aggregates from amorphous to micro-crystalline. This process causes desorption of boron, its leaching out by the waters circulating in the oxidized zone and ultimately its complete removal.

A series of experiments was performed in order to determine the content of boric anhydride in the hydrous iron oxides replacing ludwigite. At the same time, data were obtained on the variation in the amount of adsorbed boron with the degree of dehydration of the oxides and on the degree of leaching of adsorbed boron from the hydrous oxides of different compositions.

The hydrous iron oxide pseudomorphs after ludwigite always contain a certain amount of magnetite which is almost unoxidized, and for this reason the monominerotic fraction of hydrous iron oxides was obtained by simultaneous magnetic separation and elutriation in distilled water. The monominerotic fractions of hydrous iron oxides and of magnetite as well as the distilled water in which the fractions were separated were analyzed for boric anhydride. It was noticed that the magnetite fraction contained no boron, or only traces of it, due a slight admixture of goethite. In the experiments on the degree of leaching of boron from hydrous iron oxides of different compositions, weighed samples of the monominerotic fraction were stirred in water for 1/2, 1 and 2 hours, and the amount of boron which passed into solution was determined. The results of these analyses are given in Table 2.

The data of Table 2 show that during the separation of monominerotic fractions of goethite and magnetite, 37% of the total amount of boron anhydride contained in goethite passed into solution, that 80-85%  $B_2O_3$  passed into solution during the first half hour of stirring and that further stirring

\* Analyses for boron anhydride in iron hydroxides were made by the associates of the Institute of Geochemistry and Analytical Chemistry, N. N. Ryugina and G. E. Kuril'chikova.

Table 2

Content and Leaching of Adsorbed Boron  
from Hydrous Iron Oxides

Composition of hydrous iron oxides formed after ludwigite	Boron anhydride content, %					after stir- ring for 30 min	1 hour	2 hours			
	in mono- mineralic fraction of hydrous oxides	in solution									
		after sepa- ration of fractions	after stirring for								
Yellow-brown goethite with a greenish cast	2.30	0.86	1.95	1.82		Not determ.					
Yellow-brown goethite	1.93	0.69	1.27	1.30	1.32						
Yellow-brown goethite with reddish cast	1.09	0.40	0.88	0.88		Not determ.					
Reddish-brown hydro- hematite	0.38	0.17	0.23	0.38		Not determ.					

produced practically no change. In the case of hydrohematite, 45% B<sub>2</sub>O<sub>3</sub> passed into solution during the separation of the monomineralic fraction and further stirring resulted in complete removal of boron from hydrohematite.

It may be concluded, therefore, that as the hydrous iron oxides formed after ludwigite change to less hydrated varieties and the degree of crystallinity of the originally colloidal substances increases, boron becomes more and more desorbed.

The process of dehydration of the hydrous iron oxides is to be explained most probably not by changes in temperature and moisture content but by "ageing" of the colloids, as shown by the work of Weiser [7]. This explains the dominant role of hydrohematite in the oxidized zone and the sharp decrease in the adsorption capacity of the hydrous oxides with dehydration.

Under supergene conditions, ascharite also becomes unstable and is replaced by calcite, so that ascharitized ludwigite ores acquire a superficial crust of completely carbonatized ascharite. As in the case of replacement of ludwigite by hydrous iron oxides, boron is carried out by ground waters without forming secondary concentrations. Intensively carbonatized ascharite ore bodies are known at the Inder deposit of sedimentary borates [8].

The altered ludwigite ores in the oxidized zone are represented by limonites retaining the radiated structure of ludwigite, while the ascharitized varieties of ludwigite ores are altered by supergene processes into dark-gray to black aggregates of fine-grained magnetite with a certain amount of calcite.

In examining the above described process of mineral formation as a whole, it is important to note that it is characterized by a sequence of

paragenetic changes occurring with falling temperature and increasing concentration of carbon dioxide in the hydrothermal solutions. First ludwigite becomes ascharitized and later ascharite is replaced by gangue minerals (serpentine, leichtenbergite and others). The formation of the latter minerals is accompanied by removal of a number of components, notably of boron, which is carried out beyond the boundaries of the ore body without forming new minerals, and only occasionally appears in the form of datolite. Under supergene conditions ludwigite is replaced by hydrous iron oxides, and ascharite, by calcite. This process is accompanied by intensive removal of boron and its partial adsorption on the hydrous iron oxides. In conclusion, the author expresses his thanks to V. V. Shcherbina, V. L. Barsukov and N. N. Deryugina for their attention and aid during the course of this investigation.

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Received for publication  
June 9, 1958.

# EPIGENESIS IN THE QUATERNARY DEPOSITS OF NORTHERN KAZAKHSTAN

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Investigations of the epigenetic processes are especially needed at present in connection with the wide application of geochemical methods in exploratory geological work. The characteristic feature of epigenesis is the regular variation of its geochemistry with geographical zones. This enabled Fersman [1, 2, 3] to outline a scheme of latitudinal geochemical zonation of epigenesis. Later, B. B. Polynov [4, 5] created the science of geochemical landscapes which is being developed now by A. I. Perl'man [6] and other students and followers of Polynov. In recent years, detailed studies of the geochemistry of some epigenetic processes have been made by V. V. Shcherbina [7].

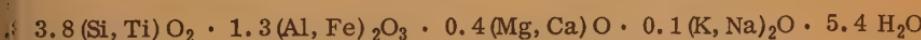
The present paper reports the results of an investigation of some epigenetic phenomena in the unconsolidated surface deposits in the steppes of Northern Kazakhstan.

## Composition of the Quaternary Deposits and Conditions of Their Epigenesis

The investigated region lies in the Ishim-Irtysh interfluve to the south of the latitude of Petropavlovsk and is known as the Ishim steppe. The central and western part of the region (North Kazakh upland) is a domical uplift of the Lower Paleozoic folded basement plunging steeply under Tertiary deposits of the West Siberian lowland and the Irtysh plain. The bedrock of the North Kazakh upland and of the adjacent plains is covered by Quaternary deposits. The greater part of the area of Northern Kazakhstan is covered by Quaternary silts of diverse origin. Comparison of the mineralogical composition of silts of the same genetic type clearly shows a difference between the sand-silt fraction from the silts of the North Kazakh upland and of the adjacent ancient alluvial and fluvioglacial plains. In the silts of the North Kazakh upland the content of quarts is lower while the content of feldspars and lithic fragments is higher. In the central, most strongly dissected part of the upland, the heavy fraction is enriched in hornblende. In the area of the piedmont plains encircling the upland, hornblende is subordinate to epidote. The surface silts of the Irtysh plain and of the West Siberian lowland contain kyanite and staurolite, which are practically absent

from the heavy fraction of the Quaternary deposits of the Kazakh hills. At first glance, the fact that the composition of the colloidal-dispersed material of the Quaternary deposits (particles less than one micron in diameter) is the same in the different genetic types, both in the Kazakh hills and on the adjacent old alluvial plains, appears to contradict the data cited above. A brief account of an investigation of the colloidal-dispersed fraction of the Quaternary deposits of Northern Kazakhstan is given below, inasmuch as this fraction plays an important part in the epigenesis of the Quaternary deposits.

Chemical analyses of ten samples of the colloidal dispersed fraction from different genetic types of Quaternary silts from different regions of Northern Kazakhstan deviate only slightly from the empirical formula:



(The formula was derived from the average values of molecular proportions in ten samples.)

The thermal curves of the colloidal-dispersed material recorded for seventeen samples of different genetic type in the laboratory of the All-Union Institute of Mineral Raw Materials are characterized by the following thermal effects:

- 1) well defined endothermic effect between 140 and 160°C;
- 2) well defined endothermic effect between 568 and 587°C;
- 3) weak endothermic effect between 862 and 881°C;
- 4) weak exothermic effect between 900 and 950°C.

These data indicate that the minerals composing the colloidal-dispersed fraction belong to the hydromica group. This is confirmed by the results of x-ray analyses of 22 samples made by Associate of the Institute G. A. Sidorenko. The powder photographs have the following characteristics:

- 1) the lines are sharper and more numerous and the background fainter as compared with the powder photographs of the montmorillonite group of minerals;
- 2) sharp reflections corresponding to the interplanar distances 3.30 Å and 4.45 Å are always present.

These characteristics indicate that the minerals of the colloidal-dispersed fraction belong to the hydromica group. Variation in the number and intensity of lines on the powder photographs of different samples indicates that the hydromicas are not equally hydrated in all samples.

Intensive hydration of the hydromicas in the colloidal-dispersed fraction is clearly indicated by crystallochemical recalculations of chemical analyses. They show that from 69 to 75% of the alkali ion positions in the crystal lattices of the hydromicas are occupied by hydroxyl ions.

The refractive indices measured on 40 samples of the colloidal dispersed fraction vary within the following limits:

$$\begin{aligned} N_g' &= 1.556 -- 1.579 \\ N_p' &= 1.539 -- 1.550 \\ N_g' - N_p' &= 0.016 -- 0.023 \end{aligned}$$

There are two possible explanations for the almost complete similarity of the mineralogical compositions of the colloidal-dispersed fractions in different genetic types of the Quaternary deposits in spite of different compositions of the sand and silt particles ( $> 0.01$  mm).

The identical mineralogical composition of particles less than one micron

in diameter may be the result of epigenetic alteration ("weathering") of the silicates of the parent rocks under definite surface conditions (climate, ground water, soils, etc.). This point of view is held by many soil scientists. Thus the latest work on this subject by E. A. Yarilova and E. I. Parfenova [8] leads them to the conclusion that a considerable part of the colloidal-dispersed fraction in the soils of the temperate zone is represented by epigenetic minerals of the hydromica type formed as a result of weathering.

A contrary view is held by most Quaternary geologists, who ascribe the similarity of the mineralogical composition of the fine fractions to sedimentation processes. The particles under one micron in diameter could have settled either from an aqueous medium an intermittent water bodies (alluvial hypothesis) or from the air, over a long period of time, in the form of atmospheric dust (eolian hypothesis). At present the problem of genesis of the clay particles in the Quaternary deposits cannot be solved, although the importance of epigenesis in the formation of the mineral assemblage of the colloidal-dispersed fraction of the Quaternary deposits is no longer in doubt.

#### Epigenetic Products in the Quaternary Deposits of Northern Kazakhstan

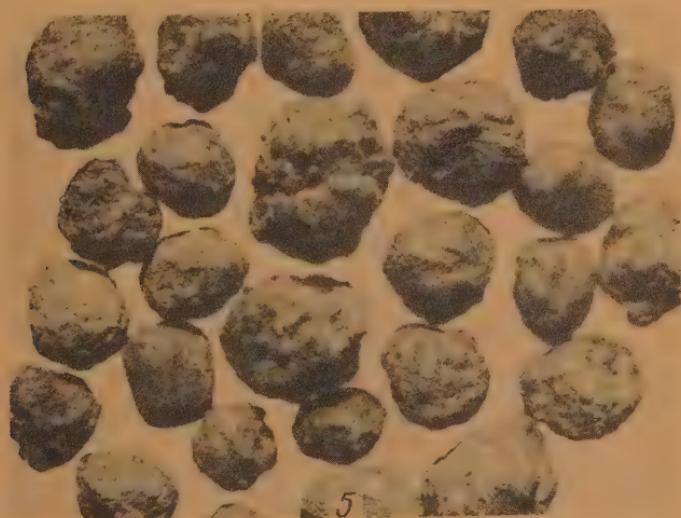
The composition and character of the products of epigenesis varies with the conditions existing in different natural zones [9, 10].

Among the calcareous epigenetic structures, widespread in the Quaternary deposits of Northern Kazakhstan, are the so-called "white eyes," friable spherical segregations of powdery calcium carbonate from 0.5 to 2.0 cm in diameter. Less common are dense concretions ("loess puppen") characteristic of the more northerly zone [11, 12] (Figs. 1 and 2).

In the gravelly varieties of Quaternary silts, in the environment of semiarid and arid steppes, epigenetic carbonates do not form concretions but occur as calcareous "whiskers" on the lower surfaces of the pebbles (Fig. 3). The colloform structure of the crypto-crystalline calcium carbonate forming "whiskers" and concretions is revealed in thin sections.

The extremely small size (usually 0.01 - 0.005 mm and less) of the crystalline particles in most of the epigenetic structures makes it impossible to separate them in absolutely pure form by any mechanical means. To study the chemical composition of the epigenetic structures, it was necessary to leach them and analyze the extracts, because, owing to the presence of varying amounts of the enclosing rocks, analyses of the structures as a whole invariably gave false results and made comparison of analyses impossible. The method of leaching with 10% hydrochloric acid (preceded and followed by treatment with 10% solution of soda) used in soil studies was selected.

In order to evaluate the effect of 10% HCl on the particles of Quaternary silt present in the structures as a mechanical admixture, the stability of the principal components of the silts (sand-silt fraction and colloidal-dispersed fraction) in 10% hydrochloric acid was investigated. The scope of this paper does not permit an account of these experiments. It will be stated only that the solubility of the mechanical admixture does not exceed 1% and frequently amounts to a fraction of one percent (or the weight of the sample). Therefore, in spite of a certain inaccuracy, the data obtained



1. Calcareous concretions (oval) from the surface silts (x2).  
Village of Bes-Tope, Akmolinsk district
2. Calcareous concretions (complex forms) from alluvial  
silts of the Solyanka River (natural size), Village of Privol'noe,  
Kokchetavsk district
3. Calcareous "whiskers" on a pebble from water-deposited  
silts on the slope of an erosional remnant (natural size). Village  
of Stalinskii, Akmolinsk district
4. Gypsum concretion from surface silts (x2.5). Village of  
Sladkovodskoe, Pavlodar district
5. Manganese concretions from surface silts (x10). Seven  
km west of the village of Bes-Tope, Akmolinsk district

Table 1

Analyses of Different Types of Calcareous Epigenetic Structures  
From the Quaternary Deposits

Components	Content, wt. %			Recalculated to 100% of epigenetic material		
	loess puppen	"white eyes"	calcareous "whiskers"	loess puppen	"white eyes"	calcareous "whiskers"
CO <sub>2</sub>	21.62	31.02	39.80	36.02	40.45	41.34
H <sub>2</sub> O-100°	1.82	2.47	1.15	-	-	-
H <sub>2</sub> O+100°	0.65	not determ.	1.58	1.08	not determ.	1.64
Extracted with 10% Na <sub>2</sub> CO <sub>3</sub>						
SiO <sub>2</sub>	0.40	0.55	0.68	0.66	0.72	0.70
Al <sub>2</sub> O <sub>3</sub>	none	none	none	-	-	-
Fe <sub>2</sub> O <sub>3</sub>	none	none	none	-	-	-
Extracted with 10% HCl						
SiO <sub>2</sub>	0.51	1.09	0.71	0.84	1.42	0.73
TiO <sub>2</sub>	traces	traces	traces	-	-	-
Al <sub>2</sub> O <sub>3</sub>	1.44	0.80	0.21	2.39	1.04	0.22
Fe <sub>2</sub> O <sub>3</sub>	2.41	0.85	0.35	4.01	1.11	0.36
CaO	28.04	38.50	50.36	46.74	50.20	52.31
MgO	1.70	1.35	0.68	2.67	1.78	0.70
SrO	traces	traces	traces	-	-	-
Na <sub>2</sub> O+K <sub>2</sub> O	0.87	0.87	1.45	1.44	1.15	1.50
Extracted with 10% Na <sub>2</sub> CO <sub>3</sub>						
SiO <sub>2</sub>	2.50	1.66	0.48	4.15	2.15	0.50
Total	33.41	3.20	1.87	5.65	4.29	1.93
mobile SiO <sub>2</sub> *						
Insoluble residue	38.40	22.53	3.35	-	-	-
Total	100.36	101.69	100.80	100.00	100.00	100.00

\* Total SiO<sub>2</sub> in the leachings

give a good idea of the composition of the epigenetic structures and permit comparison with analogous soil structures described in pedagogical literature.

The results of chemical analyses of the main varieties of calcareous structures are given in Table 1.

Very interesting is the presence in the epigenetic calcareous structures

certain elements which are never found in carbonates. Evidently these elements were captured by the epigenetic structures during the process of solution and replacement of the colloidal-dispersed fraction. Especially high is the content of silica (over 5% of the epigenetic substance).

Besides the captured rock-forming elements, a number of minor elements also owe their presence to the metasomatic and colloidal processes.

The spectrographic analyses were made in the laboratory of the All-Union Institute of Mineral Raw Materials under the supervision of A. K. Danov, by the method he developed. The accuracy of determination for most of the trace elements was  $0.5 \cdot 10^{-3}\%$ . For zinc and lead it was  $1 - 0.005\%$ ; for barium, strontium and lithium,  $0.05 - 0.01\%$ . The data of the spectrographic analyses are presented in Table 2.

Epigenetic gypsum structures. The content of epigenetic structures of gypsum in the Quaternary deposits of Northern Kazakhstan increases gradually from northwest to southeast.

The epigenetic structures of gypsum are mostly of concretionary-retentionary type (Fig. 4).

In the gravelly varieties of the Quaternary deposits, fringe-like growths form on the lower surfaces of the pebbles, which differ from the carbonate "whiskers" by their larger size.

The gypsum structures contain (see Table 3), although in smaller amounts than the carbonate structures, a number of elements which are not fixed in the crystal lattice of gypsum (aluminum, iron, and especially silicon).

The epigenetic structures of gypsum contain a smaller amount of trace elements than the carbonate structures.

Molybdenum ( $\text{m} \cdot 10^{-3}\%$ ), beryllium ( $\text{m} \cdot 10^{-3}\%$ ), yttrium ( $\text{m} \cdot 10^{-3}\%$ ) and  $10^{-3}\%$ ) were found only in the gypsum structures collected from the Quaternary deposits overlying ore deposits.

Sulfate-Chloride Water-Soluble Structures. The most widespread mineral in the structures of this group is halite. It constitutes the larger part of the sulfate-chloride structures and occurs in minute (hundredths of a millimeter) segregations or cubic crystals hundredths and tenths of a millimeter on the side; its refractive index is  $1.544 \pm 0.003$ .

The composition of halite is as follows:

CaO	.....	0.34%
MgO	.....	0.24%
BaO	.....	None
SrO	.....	None
SO <sub>3</sub>	.....	0.67%
Na	.....	36.28%
K	.....	0.72%
Cl	.....	56.25%
H <sub>2</sub> O-100°	.....	1.21%
H <sub>2</sub> O+100°	.....	2.83%
Residue insoluble in water	.....	0.27%
	Total	98.81%

Astrakhanite and epsomite are present in considerably smaller amounts. Immersion mounts these minerals appear as colorless particles tenths of a millimeter or less in size and free of any inclusions.

Infrequently a mineral similar to wattevilleite (a hydrous sulfate of

Table 2

Trace Elements in the Epigenetic Structures  
of the Quaternary Deposits of Northern Kazakhstan

Ele- ments	Epigenetic structures				Content of trace elements in $1 \cdot 10^{-3}\%$
	ferruginius	manganese	calcareous	gypsum	
Mn	10—400	400—300	1—300	1—40	1—5*
Ti	50—over 1000	20—30	1—400	5—4000	1—5*
V	10—30	1—50	5—2,3	1—10	—
Ni	2—10	5—30	0,5—2,3	0,5—1*	—
Co	1—5	—	1—400*	0,5—1*	—
Cr	5—50	—	5—40*	40*	—
Zr	5—50	2,3—20—30	4—10	1—10	—
Cu	5—30	5—40	5—40	—	—
Pb	5—30	20—50	5—10*	—	—
Sn	0,5	—	0,5—1*	—	—
Ga	2—3	1*	1*	1*	—
Be	1—5	0,5*	0,5—1*	—	—
Sr	100	100—300	100—4000	100—4000	100
Zn	5—30*	40*	50*	—	—
Sc	5*	5	5—10	—	—
Y	5—10*	5	5*	—	—
Yb	2—3*	1—3	1—2—3*	100*	100*
Ba	—	200—300	100*	—	—
Mo	—	40	—	100*	—
Li	—	—	—	5—10*	—
La	—	—	—	—	—

\* Elements not occurring in all samples

Analyses of Different Types of Gypsum Epigenetic Concretions  
From Quaternary Deposits

Components	Content, wt. %			Recalculated to 100% of epigenetic material	
	Gypsum concret.	Gypsum "whiskers"	Gypsum concretions	Gypsum "whiskers"	
$H_2O - 100^*$	5,44	5,50	—	—	0,41
$H_2O + 100$	14,10	14,08	15,68	14,95	—
n. n.	0,90	0,92	1,00	0,97	15,92
Extracted with 10% HCl					
$SiO_2$	0,45	0,41	0,47	—	—
$TiO_2$	Traces	Traces	—	—	—
$Al_2O_3$	0,19	Traces	0,24	—	—
$Fe_2O_3$	0,30	0,34	0,33	0,36	—
$CaO$	31,60	33,19	35,14	35,22	—
$MgO$	0,26	0,46	0,29	0,47	—
$SO_3$	42,25	44,68	46,97	47,53	—
Extracted with 10% $Na_2CO_3$					
$SiO_2$	0,49	0,66	0,24	0,69	—
Total mobile	0,34	0,77	0,38	0,80	—
$SiO_2^*$	5,50	0,43	—	—	—
Insol. res.	100,88	100,07	100,00	100,00	100,00

\* Total  $SiO_2$  in the leachings.

sodium and calcium) is found. Together with halite, astrakhanite and epsomite, it occurs in friable nest-like segregations and with halite forms white colloform structures 1 to 2 mm in diameter. In immersion mounts it exhibits (011) cleavage. The extinction angle  $Z_c$  is about  $30^\circ$ ; the axial angle  $(-2V)$  is near  $60^\circ$  (estimated from interference figure). Dispersion of the optic axes is distinct with  $V > r$ . The refractive indices are:

$$\begin{aligned} N_g' &= 1.466 + 0.003 \\ N_p' &= 1.433 - 0.003 \\ N_g' - N_p' &= 0.033 \end{aligned}$$

The chemical composition of the extracts from the colloform structures is as follows:

$\text{Na}^+$	---	30.86%
$\text{K}^+$	---	0.66%
$\text{Cl}^-$	---	43.13%
$\text{MgO}$	---	3.77%
$\text{CaO}$	---	2.50%
$\text{SO}_3$	---	10.26%
$\text{H}_2\text{O}-100^\circ$	---	7.14%
$\text{H}_2\text{O}+100^\circ$	---	2.20%
Total		100.52%

Recalculation of the chemical analyses into molecular proportions shows that the colloform water-soluble structures contain about 70% halite and only 30% hydrous sulfates of sodium, magnesium and calcium of the type of wattevilleite and astrakhanite.

Spectrographic analyses show that the water soluble epigenetic structures contain very small amounts of admixed elements (Table 2). Moreover, most of these are common rock-forming elements. For example, the content of silicon varies from  $5 \cdot 10^{-4}$  to about 1%; of aluminum, from  $1 \cdot 10^{-3}$  to about 1%; and of iron and manganese from  $5 \cdot 10^{-4}$  to  $1 \cdot 10^{-3}\%$ . The sulfate-chloride epigenetic structures from the Quaternary deposits lying in the vicinity of ore bodies contain barium (0.1%), vanadium ( $2-3 \cdot 10^{-3}\%$ ), molybdenum ( $5 \cdot 10^{-4}\%$ ) and copper ( $2-3 \cdot 10^{-3}\%$ ).

Ferruginous epigenetic structures are of limited distribution in the steppes of Northern Kazakhstan.

They are relatively more abundant in the old alluvial sandy deposits but are relict structures in part. The ferruginous formations (friable accumulations, less commonly concretions) are composed partly of cryptocrystalline hydrogeothite but mainly of iron silicates of the ferri-halloysite type with refractive index of 1.66-1.69.

The chemical analysis (Table 4) shows that the ferruginous epigenetic structures contain abundant admixtures (about 20% of the total mass).

Molybdenum ( $1 \cdot 10^{-2}\%$ ), antimony ( $5 \cdot 10^{-3}\%$ ) and arsenic (0.1%) were in the epigenetic ferruginous structures of Quaternary silts overlying ore bodies.

The epigenetic manganese structures, like the ferruginous, have a subordinate position among the epigenetic structures in the Quaternary deposits of Northern Kazakhstan. The manganese structures are friable, poorly cemented segregations ("spots") or small concretions from 1 to 3 mm in diameter (Fig. 5). In a number of cases, manganese concretions are relicts of a moister environment.

Table 4

Analysis of a Ferruginius Concretion  
From the Old Alluvial Sands

Components	Content, wt. %	Recalculated to 100% of epigenetic material
In the initial material		
H <sub>2</sub> O-100°	0.51	-
misc.	4.23	19.84
MnO	0.50	2.29
MnO <sub>2</sub>	none	-
Extracted with 10% Na <sub>2</sub> CO <sub>3</sub>		
SiO <sub>2</sub>	1.40	6.42
Al <sub>2</sub> O <sub>3</sub>	0.16	0.73
Fe <sub>2</sub> O <sub>3</sub>	traces	-
Extracted with 10% HCl		
SiO <sub>2</sub>	0.76	3.50
TiO <sub>2</sub>	0.07	0.32
Al <sub>2</sub> O <sub>3</sub>	0.24	1.10
Fe <sub>2</sub> O <sub>3</sub>	13.00	59.31
CaO	0.25	1.15
MgO	0.40	1.80
BaO	none	-
NiO	none	-
Na <sub>2</sub> O	0.38	1.74
K <sub>2</sub> O	none	-
Extracted with 10% Na <sub>2</sub> CO <sub>3</sub>		
SiO <sub>2</sub>	0.40	1.80
Al <sub>2</sub> O <sub>3</sub>	none	-
Fe <sub>2</sub> O <sub>3</sub>	none	-
soluble fraction	21.79	-
misc. + MnO		-
soluble residue	79.50	-
total	101.80	100.00

Minor Elements in the Quaternary Deposits  
of Northern Kazakhstan

The Quaternary deposits of Northern Kazakhstan contain a definite assemblage of trace elements. Table 5 presents comparative data on the average content of trace elements (i. e. ratios of the sum of the results of petrographic analyses to the number of samples) in the Quaternary deposits as a whole and in their colloidal-dispersed and clastic fractions. The data show that the content of elements intermediate between rock-forming

Table 5

Variation in the Content of Trace Elements  
in the Main Components of the Quaternary Deposits  
of Northern Kazakhstan  
(based on about 200 spectrographic analyses)

Elements	Average content, $1 \cdot 10^{-3}\%$		
	In total samples of Quaternary deposits	In samples of colloidal-dispersed fraction	In samples of detrital quartz from Quaternary deposits
Ti	405	30	8
Mn	112	77	9,6
V	12	11,3	0,7*
Cr	8,2*	11,2	—
Zr	6,8	7,2	0,8**
Ga	4,3	6,3	1 (?)**
Be	0,8**	1,0*	—
Sc	5,2*	9,5	—
Pb	9,4*	7,7*	2
Zn	8,4*	15	—
Cu	6,8	10,7	0,8*
Ag	0,5**	0,5**	—
Mo	0,7**	0,9*	—
Ni	2,1	2,5	—
Co	1,2	0,9	—
La	5,0**	5,0*	—
Y	5,0	5,0	—
Yb	2	1,7	—
Li	100 (?)	100 (?)	—
Sr	123 (?)	100 (?)	100 (?)
Ba	136 (?)	100 (?)	—
Sn	0,5**	0,9*	—
Nb	5 (?)**	5 (?)*	—

\* Elements frequently found by spectrographic analysis.

\*\* Elements infrequently found.

Note: Comma represents decimal point.

and minor elements (titanium and manganese) is lower in the colloidal-dispersed fraction. The content of trace elements in this fraction and in the total samples is approximately of the same order.

It must be noted that according to spectrographic analysis the following elements are absent from all samples of the Quaternary deposits: tungsten, niobium, tantalum, cadmium, germanium, indium, cerium, gadolinium, scandium, platinum, thallium, cesium, tellurium and rhenium.

The mineralogical and geochemical peculiarities of the colloidal-dispersed fraction favor concentration of dispersed elements. In the well-known monograph devoted to the distribution of minor and dispersed elements in soils, Academician A. P. Vinogradov [13] emphasizes the importance of the occurrence of these elements in the adsorbed state in soils and oil-forming rocks. The data from Northern Kazakhstan (Table 5) strongly confirm this view. It must be borne in mind that spectrographic analyses are made on samples of the colloidal-dispersed fraction separated by a method insuring complete removal of weakly bonded elements. Separation of particles smaller than one micron is possible only after complete removal of calcium, which tends to coagulate them. Calcium was removed either by prolonged action of sodium chloride solution, followed by washing the material in distilled water, or by solution in 0.1 N hydrochloric acid, followed by boiling and addition of a few drops of ammonium hydroxide. In such cases, only those elements were left in the colloidal-dispersed fraction which are strongly held by adsorption or by other surface forces, and whose content in the hydromicas increases with the degree of replacement of the alkali ions by the hydroxyl.

The study of the behavior of trace elements during epigenesis is very important, especially in light of the latest data on the deviations in their behavior from certain chemical regularities [14].

To study the effect of soil formation on the distribution of trace elements, spectrographic analyses were made on samples from the different horizons of typical Northern Kazakhstan soils. Profiles of the following soils were studied: southern chernozem (9 profiles), saline chernozems from small depressions (2 profiles), and gray forest soils (2 profiles). The results of these analyses are given in Table 6.

Table 6

Average Content of Some Trace Elements  
in the Southern Chernozems of Northern Kazakhstan,  $1 \cdot 10^{-3}\%$

Soil horizons	Ti	Mn	Co	Ni	V	Zr	Sc	Zn	Cu	Pb	Ga
Horizon A	205	114	1,4	1,6	40	5,9	5,0	6,7	4,2	6,6	2,1
Horizon B	461	134	1,5	2,0	11	8,6	6,0	4,4	4,5	10,0	2,7
Horizon C	344	114	1,2	2,0	10	6,3	5,0	7,0	6,6	11,0	4,5

Note: Comma represents decimal point.

These results show that the southern chernozems accumulate (in horizon A) titanium, manganese, cobalt, nickel, vanadium, zirconium and scandium, while gallium, lead, copper and zinc are leached out, although zinc is

relatively enriched in the humic horizon.

Beryllium, lanthanum, yttrium, ytterbium, lithium, strontium, barium and tin are uniformly distributed through the soil profile. The distribution of molybdenum, silver, tin, arsenic and antimony was not ascertained because the content of these elements was below the limit of sensitivity of the spectrographic method.

Rare earths, lithium, barium and nickel are uniformly distributed through the profiles of the analyzed saline soils. The content of manganese, titanium, cobalt, vanadium, zirconium, zinc, copper, gallium and lead decreases in the soils, but the last three elements are relatively enriched in the hardpan.

A considerably different distribution of trace elements was found in the podzols under thick forests. Podzolization is especially clearly marked in the skeletal soils under pine forests. In these soils, zinc and manganese are accumulated in the humic horizon; the content of cobalt, gallium, ytterbium, molybdenum, copper and lead is diminished, and these elements are concentrated in the illuvial zone, which is sometimes structureless. The only element which shows a slight tendency towards accumulation in the leached horizon is zirconium. Titanium, vanadium, chromium, tin, scandium, lanthanum, yttrium, strontium, barium and lithium are uniformly distributed through the profiles of the forest soils.

The distribution of beryllium is not clear.

The data given in Table 6 indicate that the effect of the formation of a soil profile on the redistribution of trace elements in the steppe environment is not great. The variation in the content of trace elements with the horizon in the soil profile does not affect the content of these elements in the soil-forming rocks of the Quaternary deposits. Judging by the published data [13, 15], the effect of the soil-forming process is greater in the humid zones (taiga-podzol zone and the tropical and subtropical forest zones).

The physicochemical processes occurring outside of the humic soil horizon (the epigenetic processes in the Quaternary deposits) have a much stronger effect on the redistribution of trace elements. During epigenesis some of the elements become mobile. There are two ways in which this may happen. First, the minerals which are metastable under surface conditions are decomposed by chemical weathering. Second, the colloidal-dispersed fraction of the Quaternary deposits is destroyed by the replacement of the fine clay particles by some of the epigenetic structures. As a result of these processes, a considerable amount of silicon, aluminum, iron, calcium, magnesium, potassium and sodium becomes mobile. Not all of these elements form new minerals. A part of the content of the element persists in uncombined form. Study of epigenesis in the Quaternary deposits of Northern Kazakhstan shows that calcium, aluminum and potassium accumulate as admixtures in the epigenetic structures (Table 7) and are evidently removed, to a considerable extent, by surface waters.

The impossibility of separation of epigenetic material absolutely free from admixture considerably lowers the contract in the distribution of some of the trace elements. To compensate in some measure for this shortcoming, parallel analyses were made of the total sample of the deposit, of its sand-silt and finely dispersed fractions and of its epigenetic structures. As a result, it was possible, in a number of cases, to discover a tendency in some trace elements towards regular distribution among the different components of the Quaternary deposits. Even more difficult is the investigation of the form of occurrence of minor elements. Detailed microscopic examination of epigenetic structures indicates that these elements do not

Table 7

## Content of Some Elements in Mobile Form in the Different Epigenetic Structures

Epigenetic structures	Content in hydrochloric acid + soda extract in percent of epigenetic material		
	SiO <sub>2</sub>	Al <sub>2</sub> O <sub>3</sub>	K <sub>2</sub> O
Calcareous	1.93-5.65	0.22-2.39	0.01-0.1
Gypsum	0.38-0.80	0.29 and less	0.01-0.1
Sulfate-chloride	0.01-1.0	0.001-1.0	0.72
Ferruginous	11.72	1.83	n · 0.1
Manganese	more than 1.0	more than 1.0	n · 0.1

minerals. Some of the trace elements enter diadynamically into the structures of the epigenetic minerals, some exist in the mechanical admixtures of the parent rock, and evidently a considerable part of them is accumulated by surface forces (adsorption, etc.). The latter phenomenon becomes especially important in epigenesis because of the extremely small size of the crystallized individuals in the epigenetic structures and the abundance of the finely dispersed phase. These problems should be clarified to some extent by the work now being carried out with the use of the cation-dialytic method.

As was shown earlier, a large part of the minor elements in the Quaternary deposits is fixed in the colloidal-dispersed fraction. Therefore, the redistribution of the trace elements during epigenesis is determined to a considerable extent by the effect of a particular process on this fraction. A comparison of the average content of trace elements in the Quaternary deposits (Table 5) with their content in the epigenetic structures given in the description of the latter shows that there is a preferential accumulation (or rejection) of certain trace elements by the different types of epigenetic structures. The epigenetic structures produced by the replacement of the colloidal-dispersed fraction of the Quaternary deposits inherit some of its trace elements. Evidently this (together with the purely chemical phenomenon) is a partial explanation of the high content of admixed elements in the epigenetic structures that are calcareous, ferruginous and manganeseiferous as compared with the epigenetic structures of gypsum and chloride-sulfate. A clear idea of the content of individual trace elements in the general mass of the Quaternary deposits, in their components and in epigenetic structures is given by curves constructed from the data of spectrographic analyses showing variation in the content of each element. A sample variation curve is presented in Fig. 6. The average values for the content of different trace elements in the Quaternary deposits and in the different epigenetic structures, together with the variation curves, led to the following observations.

The calcareous epigenetic structures selectively accumulate strontium, to a less extent, copper, zinc, molybdenum, tin and titanium. The content of nickel, vanadium and lead in these structures is lower than in the host rock. The gypsum and chloride-sulfate epigenetic formations

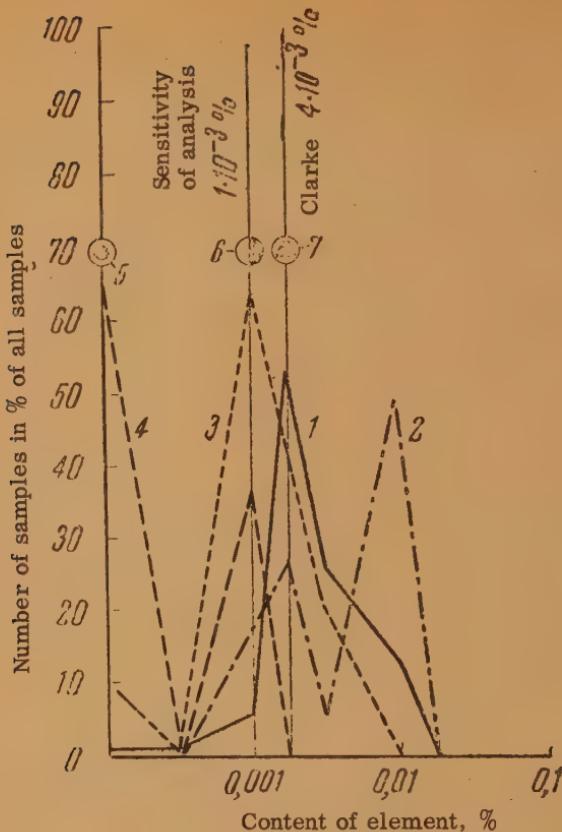


Fig. 6. Variation curves of gallium content in Quaternary deposits

1 -- content in total samples; 2 -- content in samples of colloidal-dispersed fraction; 3 -- content in calcareous epigenetic structures; 4 -- content in gypsum structures; 5 -- content in sulfate-chloride structures; 6 -- average content in manganese structures on the basis of analyses of one sample; 7 -- average content in ferruginous structures on the basis of analyses of one sample.

concentrate strontium but have a diminished content of almost all other trace elements. In the ferruginous epigenetic formations, cobalt, chromium, beryllium and molybdenum are concentrated. In the manganese formations, barium, lead, nickel, cobalt and molybdenum are selectively concentrated and the content of zirconium, chromium and zinc is diminished. The colloidal-dispersed fraction of the Quaternary deposits concentrate gallium, scandium, zinc, zirconium and vanadium.

Summary

1. The Quaternary deposits of Northern Kazakhstan are undergoing genetic change in a definite geographical environment (steppe). Of all interrelated epigenetic processes, the most important are soil formation and the formation of epigenetic minerals.
2. The soil process in the steppe zone causes a regular redistribution of elements in the soil profile. This redistribution is relatively slight. Much more significant is the redistribution of the elements due to geological processes, resulting in the formation of epigenetic structures and minerals. The epigenetic structures are concretions, crusts, powder-like accumulations and coatings. Mineralogically, these structures consist mainly of cryptocrystalline calcite and fine-grained gypsum. Halite, epsomite, astrakhanite, wattevilleite and the iron rich-halloysite group of minerals are present in smaller amounts; hydrogoethite and wad are still less abundant.
3. The composition of the epigenetic structures in the Quaternary deposits is sensitive to change in the natural landscape. In the environment of the steppe-forest subzone, calcareous epigenetic structures are dominant. In the semi-arid steppe subzone, gypsum structures predominate, and in the arid steppe subzone, the chlorine-sulfate structures increase.
4. The different epigenetic structures selectively accumulate certain trace elements. It was found that the main mass of trace elements in the Quaternary deposits occurs in the colloidal-dispersed fraction. Therefore, the greatest variety of composition of admixed elements is found in the epigenetic structures, whose origin is related, through exchange or metamorphic reactions, to the colloidal-dispersed fraction.

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Received for publication  
March 21, 1958.

## Brief Communications

# THE ISOTOPIC COMPOSITION OF LEAD FROM THE SULFIDE-BEARING PHOSPHORITES OF PODOLIYA

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The sulfide-bearing phosphorite concretions widely distributed in the Melnitskii, Vinnitskii and Chernovitskii districts of the Ukrainian SSR and in the Cambrian-Silurian thinly laminated shales abundantly represented in the Dnestr region and in Podolia. The tightly packed phosphorite concretions form individual horizontal layers traceable for hundreds of meters.

The characteristic features of the mineral assemblages in the sulfide-bearing phosphorite concretions studied by the author [1] indicate an intimate relationship between lead, zinc and copper sulfides and the calcium phosphate deposits, and point to a single process of diagenesis of the amorphous colloidal masses occurring in the reducing environment produced by the evolution of hydrogen sulfide. The author's observations suggest that sulfide-bearing phosphorite concretions formed as a result of a continuous process consisting of a series of successive stages of ageing, dehydration and crystallization of the initially gel-like phosphatic material containing besides the predominant calcium phosphate, a certain amount of heavy metals. The heavy metals, lead, copper and zinc, locally concentrated in bottom mud waters, may have been adsorbed on calcium phosphate and precipitated from the sea water together with it. This is confirmed by the absence of heavy metals in the epigenetic calcium phosphate gels. Initially the metals were in the colloidal-dispersed state. Later, as a result of crystallization, they were gathered into crystalline aggregates. The accumulation of sulfides in the centers of concretions was probably favored considerably by the observed sequence of crystallization, with the phosphatic material of the outer layers of the concretions crystallizing as galena before the other components. This was accompanied by the clearing of the growing crystal lattice of tricalcium fluophosphate of impurities and the crowding of the colloidal sulfides into the interior spaces resulting in the complete dehydration of phosphate and its change into the crystalline state.

The peculiar origin of the sulfides in the concretions of Podolian phosphorites and the predominance of lead in the sulfide assemblage made it interesting to determine the isotopic composition of lead in galena from

the cores of the concretions and compare it with the isotopic composition of the common ore lead from sulfide deposits of different genetic types.

At the author's request a mass-spectrometric analysis of lead was made by G. R. Rik at the Radium Institute, Academy of Sciences USSR.

The results showed the following isotopic composition of lead:

204	206	207	208
1	$20.18 \pm 0.1$	$15.98 \pm 0.1$	$38.09 \pm 0.2$

The general tendency of the isotopic composition of lead from lead ores to change with age is clearly presented in the tabulated data of A. O. Nier [2, 3] and A. P. Vinogradov [4]. Below, a table is presented borrowed from the work by G. R. Rik and G. V. Avdzeiko [5], in which an attempt was made to systematize the existing data on the variation in the isotopic composition of lead with geologic age.

The table gives only the average values of the isotopic composition of ore leads for the larger divisions of geologic time.

A comparison of the isotopic composition of lead from the galena of the Podolian phosphorite concretions with the data of the table shows its "anomalous" character very clearly.

It has a noticeably higher content of the radioactive lead isotopes, especially of  $Pb^{206}$  and  $Pb^{207}$ , than is to be expected in the Cambrian-Silurian leads if the average values given in the table are considered. Even the youngest Mesozoic-Cenozoic leads have lower content of these isotopes.

Geologic era	Age limits, $10^6$ years	Isotopic composition of lead		
		206/204	207/204	208/204
Archaean	1800-1000	$15.33 \pm 0.31$	$15.08 \pm 0.36$	$34.61 \pm 0.14$
Proterozoic	1000-500	$16.01 \pm 0.05$	$15.26 \pm 0.05$	$35.39 \pm 0.08$
Paleozoic	500-200	$17.64 \pm 0.10$	$15.44 \pm 0.07$	$37.57 \pm 0.14$
Mesozoic-Cenozoic	200-25	$18.42 \pm 0.10$	$15.76 \pm 0.06$	$38.76 \pm 0.12$

The "anomalous" isotopic composition of lead caused by the relative enrichment in radioactive lead isotopes is known at present for a number of deposits of different origin.

The sulfide-bearing phosphorites of Podolia contain "anomalous" lead whose isotopic composition was finally fixed in the vicinity of the uranium-rich ancient rocks of the adjacent region.

There is no reason whatever to assume the introduction of lead after the formation of the concretions.

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Received for publication  
October 29, 1958.



Geokhimiya began publication in 1956 under the able editorship of A. P. Vinogradov. It is the Soviet counterpart of Geochimica et Cosmochimica Acta, having practically identical fields of interest and coverage and publishing approximately the same number of pages per year. With the great increase in geochemical research in the U. S. S. R., there have come into being a number of highly specialized journals in geochemistry and related fields. It is probably better to begin translating this more general journal first and follow with some of the more specialized ones if interest appears to justify this course of action and if the financial arrangements can be made.

An initial grant from the National Science Foundation in 1958 enabled the Geochemical Society to translate and publish the eight issues for that calendar year. These issues have been very well received by a growing list of subscribers in most of the countries of the Western world.

Many inquiries have been received concerning back issues (1956 and 1957) and continuation of the program for issues after 1958. The National Science Foundation has made additional grants for translation and publication of the issues for 1956, 1957 and 1959. These are being translated and issued as rapidly as they can be processed. Prices are the same as for the 1958 issues (see inside front cover). Subscriptions and orders for single issues should be sent to the Geochemical Society in care of the undersigned.

The National Science Foundation has continued to be most cooperative in this venture. They are continuing support of the project although subscribers are too few to make it anything like self supporting thus far. It is hoped that subscribers will call attention of other interested workers to the availability of the translation of Geokhimiya so that these important research papers can be made more generally available to those interested in geochemical and related investigations.

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